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

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Abstract: This study was aimed at investigating the influence of different drying methods on the photochemical composition and inhibition efficiency of *Alchornea laxiflora* and *Muccuna 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 600C to obtained air dried *Alchornea laxiflora* leaves (AALL), air dried *Mucunna flagellepes* leaves (AMFL), sun dried *Alchornea laxiflora* leaves (SALL) and sun dried *Muccuna 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: Sapolin 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: Sapolin 28.55mg/g, Tannin 5.39 mg/g, Flavnoid 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, Flavnoid 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: Sapolin 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, *Muccuna 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 engage 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 use acidic solutions extensively and as such iron and steel vessels or surfaces used in these environments are prone to corrosion [5]. The use of many inorganic inhibitors, particularly those containing phosphate, chromate, and other heavy metals, is now being gradually restricted or banned by various environmental regulations because of their toxicity and difficulties faced in their disposal especially in the marine industry, where aquatic life is at threat [6]. Synthetic organic inhibitors have also been extensively applied but their use is now being marred by their toxicity and high cost of manufacturing. This has prompted researchers to explore other areas to produce eco-friendly, cheap, and biodegradable green corrosion inhibitors to replace inorganic and synthetic organic inhibitors.

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 analogous 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 product such as aroma and appearance by hindering any biochemical changes [9]. Drying can be thermally such as sun dry and oven dry or non-thermal. However, this review gives an overview of the effect of the drying method (air and sun drying) on phytochemicals and inhibitive properties of *Alchornea laxiflora* and *Muccuna flagellepes* leaves extracted with ethanol on mild steel.

2. Materials and Methods

2.1. Materials

The mild steel used for this study was procured and the chemical composition was carried out at metallurgical department, Federal University of Technology, AKure Ondo State, Nigeria. The sheets was mechanically press-cut into 4.00 x 0.08 x 5.00cm samples. A small hole of about 5 mm diameter near the upper edge of the coupons was made which help hold them with glass hooks and suspend them into the corrosive medium. The mild steel was polished with different grades of emery paper placed on a streuer polishing machine, washed with distilled water and dried with nitrogen gas before preservation in a desiccator [10-12]. The aggressive acidic solution of 1.0 M HCl was prepared by dilution of concentrated HCl with distilled water and all experiment was carried out in unstirred solutions and all weighing was taking with analytical weighing balance (Metler Toledo PB153).

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^{-1} cm^{-2}) 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).

$$CR=\frac{\Delta W}{At} \quad (1)$$

$$\text{Inhibition Efficiency} = 1-\left(\frac{CR_2}{CR_1}\right) X100 \quad (2)$$

$$\text{Surface Coverage } (\emptyset)=1-\left(\frac{CR_2}{CR_1}\right) \quad (3)$$

Where Δw is the weight loss in grams, CR_1 and CR_2 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 cm^2 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 Discursion

3.1. Phytochemical Analysis

Table 1. *Qualitative phytochemical screening of air and sun dried Alchornea laxiflora and Mucunna flagellepes leaves extracts.*

	AALL	AMFL	SALL	SMFL
Saponin	+	+	+	+
Tannin	+	+	+	+
Phylobatanin	+	-	+	-
Flavnoid	+	+	+	-
Steroid	-	-	-	-
Terpenoid	+	+	+	+
Alkaloid	+	+	+	+
Anthraquinone	-	-	-	-
Cardiac glycoside				
Legal Test	+	+	+	+
Killiani Test	+	+	+	+
Lieberman Test	-	-	-	-
Salkwoski 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)	45.55	28.55	20.00	15.00
Tannin (mg/g)	10.58	5.39	4.04	3.82
Flavnoid (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
Phytobalatin (mg/g)	2.43	-	2.57	-
Cardiac glycoside (mg/g)	4.72	6.33	3.86	4.93

The corrosion of mild steel in 1.0 M HCl solution containing plant extracts can be inhibited due to the adsorption of phytochemicals present in plant extracts through their lone pair of electrons and π-electrons with the d-orbitals on the mild steel surface [20-22]. The polar functions with S, O or N and π-electrons of the organic compounds are usually regarded as the reaction center for the establishment of the adsorption process. It is interesting to see here that all the identified compounds from plant extracts contained oxygen and/or π-electrons in their molecules. Moreover, from the previous studies on the phytochemical constituents of the plant extracts, it was established that the plant extracts used in this study also contain a mixture of organic compounds containing O, N or π-electrons in their molecules [23]. Hence, the corrosion inhibition of mild steel through these studied plants may be attributed to the adsorption of the phytochemicals containing O, N or π-electrons in their molecules as these atoms are regarded as centers of adsorption onto the metal surface. Tables 1and 2 showed the qualitative and quantitative phytochemical screening of the air dried and sun dried *Alchornea laxiflora* and *Mucunna flagellepes* 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 *Muccuna 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].

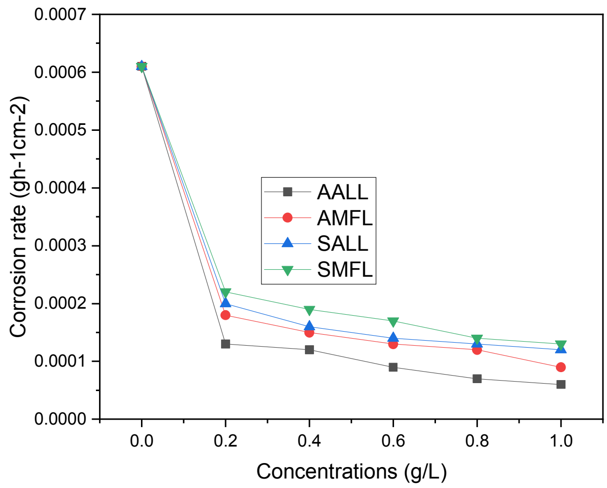


Figure 1. *Plot of Corrosion rate of mild steel in 1.0 M HCl against different Concentrations of the leaves extract.*

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].

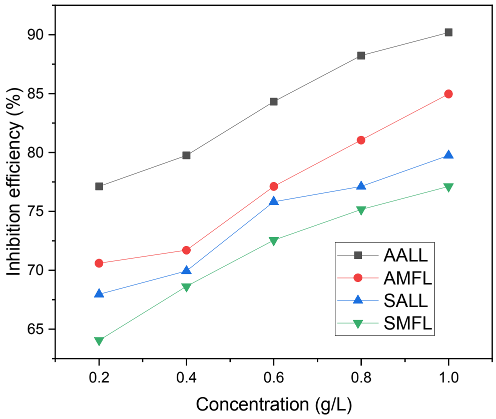
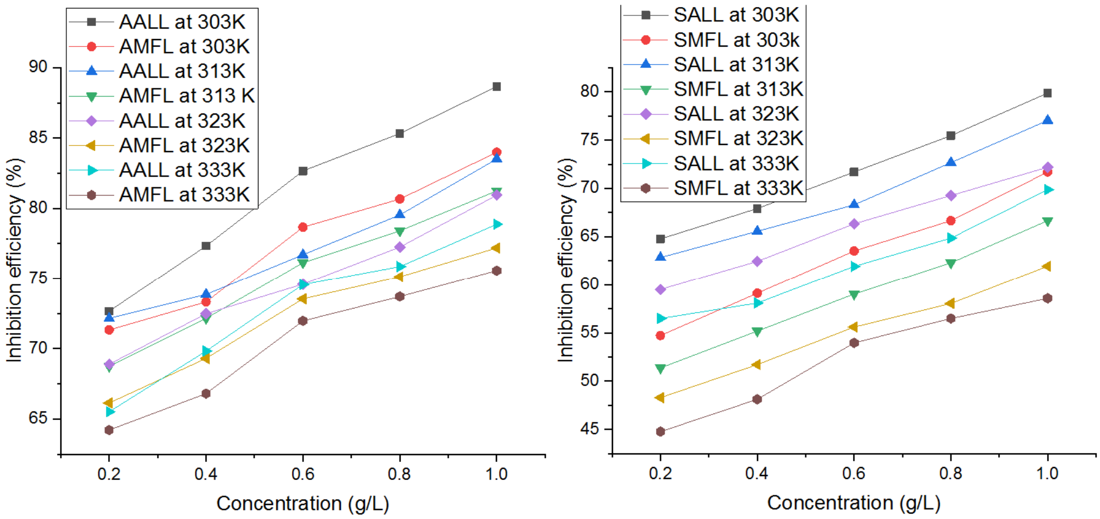


Figure 2. *Plot of Inhibition Efficiency of the air dried and sun dried leaves extracts against their Concentrations at room Temperature.*

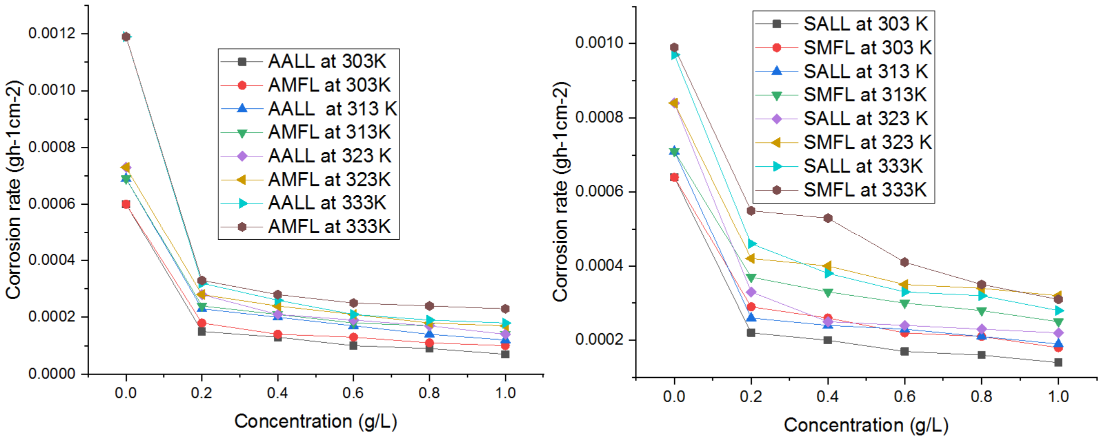
3.4. Effect of Temperature on Inhibition Efficiency

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 in 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.



(a) (b)

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



(a) (b)

Presence (a) AALL and AMFL (b) SALL and SMFL leaves extract at different Temperature.

Figure 4. *Plot of Corrosion rate of mild steel in 1.0MHCl in the absence and*

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 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_L and the weight change at time t, ($Wi-W_L$) while k, is the first order rate constant.

$$\ln (Wi\text{-}WL) = -k1\ t + \ln WL \tag{4}$$

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 (ΔH°) and Entropy of Activation (ΔS°) 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.

$$Ea = -2.303 \times R \times Slope \tag{5}$$

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 $log\frac{CR}{T}\ vs\ \frac{1}{T}$, the enthalpy change (ΔH°) for all the samples extract was obtained by using equation 6

$$\Delta H = \text{Slope x R} \tag{6}$$

where R is the gas constant (8.314)

The enthalpy (ΔH°) 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:

$$\text{Intercept} = \log\left(\frac{R}{Nh}\right) + \frac{\Delta S}{R} \quad (7)$$

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 flagellepes leaves extract.*

Time (days)	blanks	Air dried *Alchornea laxiflora* leaves extracts					Air dried *Mucuna flagellepes* leaves extract				
		0.2g/L	0.4g/L	0.6g/L	0.8g/L	1.0g/L	0.2g/L	0.4g/L	0.6g/L	0.8g/L	1.0g/L
1	0.6124	0.0764	0.0712	0.0689	0.0645	0.0593	0.2593	0.1984	0.1012	0.0952	0.0672
2	1.2247	0.1634	0.1356	0.1311	0.1283	0.0792	0.4588	0.3662	0.2338	0.2041	0.1241
3	1.7563	0.2456	0.2248	0.1837	0.1599	0.1363	0.5565	0.4560	0.3564	0.2856	0.1566
4	1.9878	0.3859	0.3762	0.2649	0.2241	0.1864	0.6584	0.5162	0.4262	0.3696	0.2057
5	2.5691	0.5163	0.4871	0.3882	0.3162	0.2482	0.7363	0.6152	0.5164	0.4263	0.2851
6	2.7706	0.6161	0.5982	0.4737	0.3792	0.3143	0.8619	0.7044	0.6024	0.5166	0.3368
7	2.8417	0.7314	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 flagellepes leaves extract.*

Time (days)	blanks	Sun dried *Alchornea laxiflora* leave extract					Sun dried *Mucuna flagellepes* leave extract				
		0.2g/L	0.4g/L	0.6g/L	0.8g/L	1.0g/L	0.2g/L	0.4g/L	0.6g/L	0.8g/L	1.0g/L
1	0.6124	0.2993	0.1852	0.1341	0.1102	0.0744	0.3561	0.2593	0.1532	0.1341	0.0812
2	1.2247	0.5233	0.4145	0.3291	0.2354	0.1564	0.5612	0.4764	0.3564	0.3247	0.2067
3	1.7563	0.6453	0.4811	0.3911	0.3371	0.2241	0.7259	0.6162	0.4463	0.3791	0.2744
4	1.9878	0.7984	0.6391	0.4892	0.3812	0.2691	0.8993	0.7667	0.5951	0.3842	0.3041
5	2.5691	0.9550	0.7491	0.5540	0.4391	0.2963	1.0347	0.9021	0.6587	0.5152	0.3563
6	2.7706	0.9932	0.8152	0.6541	0.5462	0.4162	1.2491	1.0764	0.7921	0.6044	0.5166
7	2.8417	1.1231	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 flagellepes leaves extracted with ethanol.*

Conc. (g/L)	Rate Constant (K)				Half Life (days)			
	AALL	AMFL	SALL	SMFL	AALL	AMFL	SALL	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

Which implies?

$$\Delta S = \text{Intercept} - \log\left(\frac{R}{Nh}\right) \text{ X R X2.303 X 10-3} \quad (8)$$

Where: h= plank' constant (6.62617x10-34)

N = Avogadro's number (6.022045x1023)

R = gas constant (8.314)

From the table of the result, the values obtained for entropy (ΔS) change are negative for both air dried and sun dried *Alchornea laxiflora* and *Mucunna flagellepes* 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 (θ). 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 (θ) 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 Ea, ΔH and ΔS in the absence and presence of air dried Alchornea laxiflora and Mucuna flagellepes leaves extracts at different Concentrations.*

Conc. (g/L)	Air dried *Alchornea laxifora* leaves extract			Air dried *Mucuna flagellepes* leave extract		
	Ea(Kjmol^{-1})	ΔH(Kjmol^{-1})	ΔS(Kjmol^{-1})	Ea(Kjmol^{-1})	ΔH(Kjmol^{-1})	ΔS(Kjmol^{-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 Ea, ΔH and ΔS in the absence and presence of sun dried Alchornea laxiflora and Mucuna flagellepes leaves extracts at different Concentrations.*

Conc.(g/L)	Sun dried *Alchornea laxifora* leaves extract			Sun dried *Mucuna flagellepes* leave extract		
	Ea(Kjmol^{-1})	ΔH(Kjmol^{-1})	ΔS(Kjmol^{-1})	Ea(Kjmol^{-1})	ΔH(Kjmol^{-1})	ΔS(Kjmol^{-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_f	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_f	r^2	Constant b.
303	1.145	0.998	16.1290	0.953	0.087	1.2028	0.944	30.3726
313	1.172	0.998	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_f	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_f	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 determine 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 comparism 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-Bimbi, 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. Karfa, 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. Sigircik, T. Tüken, and M. Erbil, "Assessment of the inhibition efficiency of 3, 4- diaminobenzonitrile 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 inHCl 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. Ebenso, Eco-friendly corrosion inhibitor: Inhibitive action of ethanol extracts of Garcinia kola for the corrosion of mild steel in H2SO4 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 (1^{st} 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 Phyllantus amarus as a green inhibitor for the corrosion of mild steel in H_2SO_4 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 (3), 455-459.

[17] O. O. Odeja, G. Obi, C. E. Ogwuche, 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 Ogwuche,, 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-Petiole 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 tetraoxosulphate (VI) acid environment using green corrosion inhibitors: Chysophyllum 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 Acetone 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 Aluminum. 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 riboflavin 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 Phyllantus amarus as a green inhibitor for the corrosion of mild steel in H_2SO_4 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 Thiosemicarbazon, Bulletin of Chemical Society of Ethiopia, 2004; 18 (2): 181-192.

[38] A. L. Obike, C. N. Emeruwa, V. I. Ajiwe, J. C. Igwe. Corrosion Inhibition and Adsorption Behaviour of Methanol Extract of Spondias cytherea leaves on Mild Steel Corrosion in $5.0MH_2SO_4$, 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.