Seed Shells as Active and Nontoxic Corrosion Inhibitors for Aluminum in Aggressive Acid Environments

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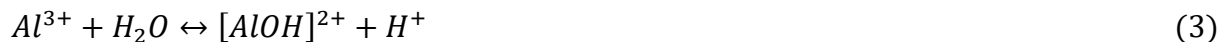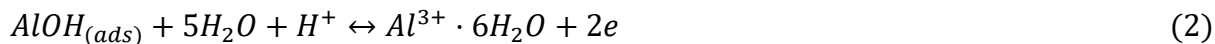*E-mail address: ln.emembolu@unizik.edu.ng

ABSTRACT

Chemical (weight loss and thermometric) measurements were used to study the corrosion inhibition characteristics of five seed shells, namely *Afzelia africana* seed shell (AASS), *Brachystegia eurycoma* seed shell (BESS), *Derium microcarpum* seed shell (DMSS), *Mucuna flagellipes* seed shell (MFSS) and *Pentaclethra macrophlla* seed shell (PMSS), respectively, on the inhibition of aluminum corrosion in aggressive 2.0% HCl solutions at 30 and 50 °C for 8 hours. Weight loss and thermometric measurements demonstrated that the seed shells (AASS, BESS, DMSS, MFSS, and PMSS extracts) act as good corrosion inhibitors. Addition of the seed shell extracts decreases the corrosion rate of the process, thereby improving inhibition performance. The result also reveals that the five seed shell extracts adsorb on the Aluminum surface through physical adsorption in accordance with Flory-Huggins and Langmuir adsorption isotherms at all temperatures investigated. Kinetic-thermodynamic parameters indicate a spontaneous adsorption process. Results of inhibition efficiency demonstrates that DMSS extract performed better as compared to BESS, AASS, PMSS, and MFSS extracts.

*Keywords***:** Aluminum corrosion, Acid inhibition, chemical measurements, seed shell extracts, thermodynamic parameters, *Afzelia africana*, *Brachystegia eurycoma*, *Derium microcarpum, Mucuna flagellipes*, *Pentaclethra macrophlla*

1. INTRODUCTION

The process of metals and its alloys returning to its natural thermodynamically stable state, known as corrosion is a natural occurrence. This decline of metals happens as a result of its interaction with environment or through chemical attack. Corrosion cannot be completely eradicated because it is a persistent and continuous problem. Thus, there is a need to develop nontoxic active corrosion inhibitors for metallic substances, and this outcome is of tremendous significance for the fortification of metal alloys and components [1, 2].

Aluminum is of great importance in this study because it is extensively utilized both, in industries and at home. The common mechanism for the dissolution of Al metal is similar to that reported by [3-6] and stated in Equations 1-5:

$$Al_{(s)} + H_2O \leftrightarrow AlOH_{(ads)} + H^+ + e \tag{1}$$

$$AlOH_{(ads)} + 5H_2O + H^+ \leftrightarrow Al^{3+} \cdot 6H_2O + 2e \tag{2}$$

$$Al^{3+} + H_2O \leftrightarrow [AlOH]^{2+} + H^+ \tag{3}$$

$$[AlOH]^{2+} + X^- \leftrightarrow [AlOHX]^+ \tag{4}$$

In the above reaction, dissolution of metal is governed by the complex reaction between the hydrated cation and anion in Equation (3), wherein the soluble complex ion produced increases the rate of metal dissolution which is dependent on the concentration of chloride – as seen in Equation (5):

$$[AlOH]^{2+} + Cl^- \rightarrow [AlOHCl]^+ \tag{5}$$
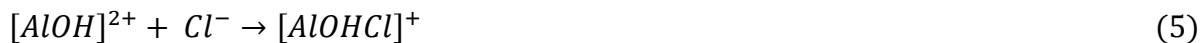
The environmental toxicity of the readily available and commonly used synthetic corrosion inhibitors has fueled the search for eco-friendly corrosion inhibitors. Several reports had equally shown that naturally occurring materials, like oil [7], leaves, stem, and roots [8-11], fruit and flower extracts [12-16] could be used as corrosion inhibitors.

Apart from being waste biomass, the potentials of shell extracts derived from *Afzelia Africana*, *Brachystegia eurycoma*, *Derium microcarpum*, *Mucuna flagellipes* and *Pentaclethra macrophlla* seeds as bio-based corrosion inhibitors effectively relate this work to the recent trend of environmental-friendly corrosion inhibitor concepts, as they are inexpensive, readily available, ecologically acceptable and renewable sources of material.

It should be recognized that the seeds of *Afzelia Africana*, *Brachystegia eurycoma*, *Derium microcarpum*, *Mucuna flagellipes* and *Pentaclethra macrophlla* are used as soup thickeners and condiments in preparing some delicacies in Eastern parts of Nigeria. Moreover, *Derium microcarpum,* popularly called 'ofor' in Igboland, is a symbol of authority.

The aim of this novel study is to investigate the inhibitive properties of five selected seed shells, namely AASS, BESS, DMSS, MFSS, and PMSS on the inhibition of aluminum corrosion in 2.0% HCl solutions, using chemical (weight loss and thermometric) techniques.

2. EXPERIMENTAL

2. 1. Materials and solution preparation

Aluminum sheets of 95% Purity were sourced from Awka, Nigeria. The Al sheets were subsequently cut into coupons for further use as previous described in [17]. All reagents and chemicals used were of analytical grade, while double distilled water was used for preparing solutions. The concentrated seed shell extracts of respective plant were employed for the preparation of inhibitor test solutions in the concentration range of 0.1% / 100 mL solution of 2.0% HCl.

2. 2. Collection of seed shells and preparation of extracts

The seed shells used in this study were derived from the seeds of *A. Africana*, *B. eurycoma*, *D. microcarpum*, *M. flagellipes* and *P. macrophlla*, as shown in **Figure 1**. The seeds were sourced from Afor Ugwuoba market, Enugu state. The seeds were cracked and the shells collected for analysis. Two hundred grams of sun dried and powdered seed shells of each plant were extracted with 95% ethanol at room temperature for 4 hours. The shell extracts of each plant were concentrated until the solvents were totally removed, as discussed previously in [17, 18]. The concentrated extracts of respective plants were kept for advance use.

2. 3. Weights loss measurements

The instruments and technique employed for weight loss measurements were as described before in [16-18]. The corrodent concentration was 0.1 % and the volume of the test solution used was 100 mL. All tests were carried out in aerated solutions. The difference between the weight at a given time and the initial weight of the coupons was taken as the weight loss that was used to evaluate the corrosion rate and inhibition efficiency for Al with different inhibitor concentrations. The process of calculation was as 2.3.1:

2. 3. 1. Corrosion rate (W)

The corrosion rate (W) was calculated using Equation (6):

$$W = \frac{M_1 - M_2}{At} \tag{6}$$

where M_1 is weight (g) before immersion, M_2 is weight (g) after immersion, A is area (cm^2) of the specimen, and t is exposure time (hours).

2. 3. 2. Inhibition efficiency ($\eta\%$)

The inhibition efficiency ($\eta\%$) of the extract was estimated using Equation (7):

$$\eta\% = \left[\frac{W_{blank} - W_{inh}}{W_{blank}}\right] \times 100 \tag{7}$$

where W_{blank} and W_{inh} are weight losses in the absence and presence of inhibitor, respectively, in HCl at the same temperature.
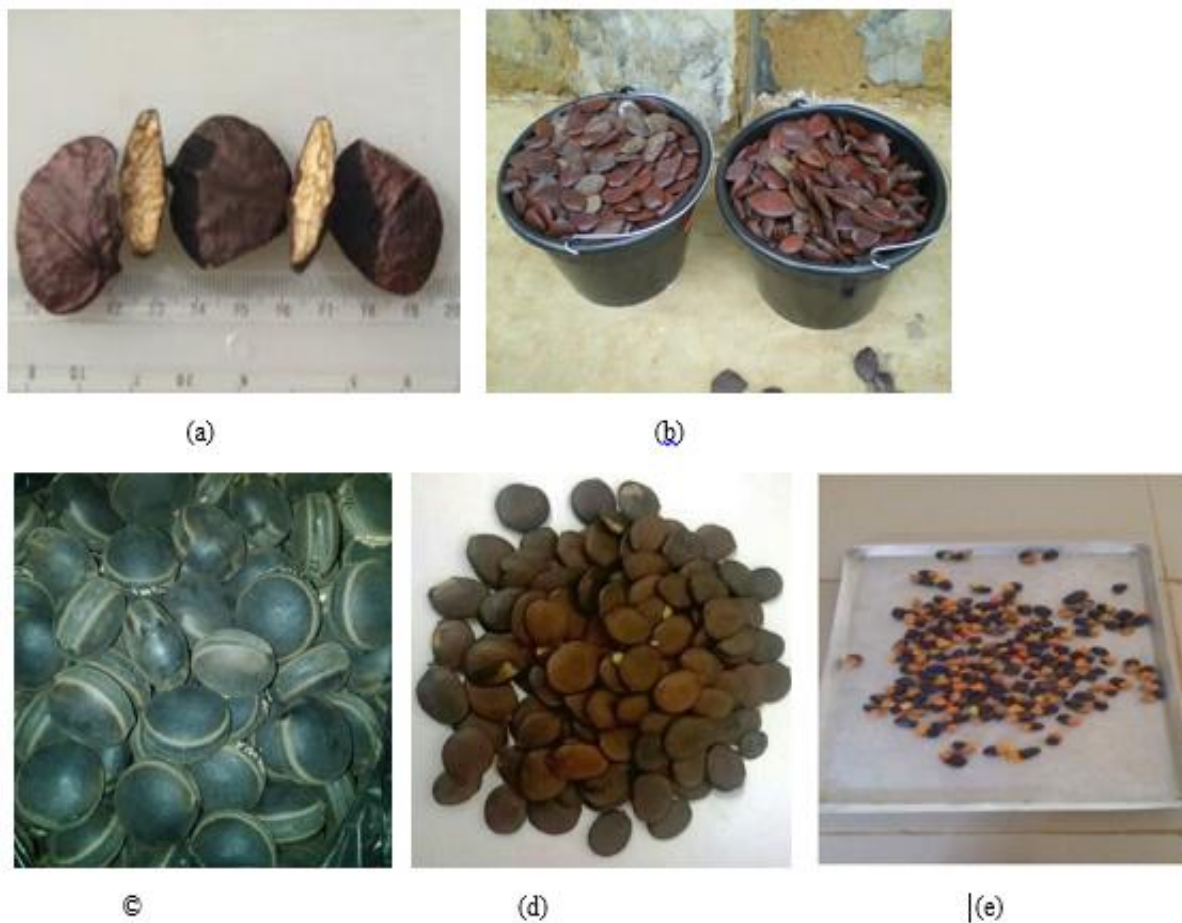
Figure 1. (a) *Derium microcarpum* (b) *Pentaclethra macrophlla* (c) *Mucuna flagellipes* (d) *Brachystegia eurycoma* (e) *Afzelia Africana* seeds

The degree of surface coverage (θ) was computed from equation (8):

$$\theta = 1 - \frac{W_{inh}}{W_{blank}} \tag{8}$$

2. 4. Thermometric method

The reaction vessel and technique for determining the corrosion behavior of Al in 2.0% HCl by thermometric measurements have been described elsewhere by other authors [3, 4]. The volume of test solution used was 70 mL, while the corrodent (HCl) concentration was held constant at 2.0% during the thermometric measurement. The initial temperature was maintained at 30°C. Advancement of the reaction process was assessed by measuring the changes in temperature with time through using a standard digital thermometer to the nearest ±0.2°C. Hence, reaction number (RN) was estimated as in (9):

$$RN(°C \ min^{-1}) = \frac{T_{max} - T_{in}}{t} \tag{9}$$

where: T_{max} and T_{in} are the maximum and initial temperatures, respectively; t is the time (min) taken to reach the maximum temperature.

The inhibition efficiency was evaluated from percentage reduction in the RN, using (10)

$$\eta\% = \left[\frac{RN_{aq} - RN_{wi}}{RN_{aq}}\right] \times 100 \qquad (10)$$

where: RN_{aq} = reaction number in the absence of inhibitor (blank solution); RN_{wi} = reaction number of 2.0 HCl containing the studied inhibitors (plant seed shell extracts), respectively.

3. RESULTS AND DISCUSSION

3. 1. Effect of time on weight loss, corrosion rate and inhibition efficiency

Aluminum coupons were exposed to the influence of aggressive acid environments in the absence and presence of different concentrations of AASS, BESS, DMSS, MFSS, and PMSS extracts for 8 hours at 30 and 50 °C temperature using the weight loss technique. Effect of time on weight loss of Aluminum coupons in HCL solutions containing different plant shell extracts at 30 and 50 °C are presented in **Figure 2**. Figure 2 depicts the gradual decrease in weight loss of the Al coupons in inhibited solutions when equated to uninhibited acid solution (blank). Close examination of the plots indicates that loss in weight of Al coupons increases as concentration of the inhibitors increases. The maximum value of weight loss was obtained at 1.64 g/L at 8 h immersion time using DMSS as inhibitor, whereas the minimum loss in weight of 0.017 g/L was obtained at 3 hours using MFSS inhibitor. Also similar graphs were obtained at 50 °C. Table 1 presents the obtained results for corrosion rates, percentage inhibition efficiency and degree surface coverage for aluminum in 0.1% HCl at 30 and 50 °C in the absence and presence of different concentrations of AASS, BESS, DMSS, MFSS, and PMSS extracts after 8 h immersion time.

The Table shows that all the plant shell extracts assessed act as inhibitors within the concentration and temperature range considered. From Table 1, it is observed that the rates of corrosion in uninhibited and inhibited systems decreased gradually with immersion time, signifying loss of strength of the aggressive solution or the gradual deposition of a protective oxide film of corrosion products on the exposed Al surfaces. Reduction in the values of Corrosion rate observed can be attributed to blocking effects of the film layers [19, 20]. Table 1 indicates vividly that in all the extracts, the inhibition efficiency increases as the concentrations and temperature increase. This can be as a result of the adsorption of the molecules of inhibitors to the metal surface – which prevents the corrodent from reaching the Al surface. The highest inhibition efficiency reached is 82.31% at 30 °C and extract concentration of 0.9 g/L, using DMSS. Phytochemical screening has revealed that AASS, BESS, DMSS, MFSS, and PMSS extracts are comprised of several mixtures of alkaloids, Tanins, saponins, flavonoids, phenolic acids, Cardiac glycoside, Terpenoids, Volatile organics and Anthraquinones [21-23, 33-40] suggesting that heteroatoms, like Nitrogen and Oxygen, contained their components. Inhibition of Al can occur due to adsorption of the plant shell extracts onto the Al surface through the active centers. Still, due to the complex nature of chemical configuration of plant shell extracts, it is difficult to assign the inhibitive effect to a particular phytochemical constituent.
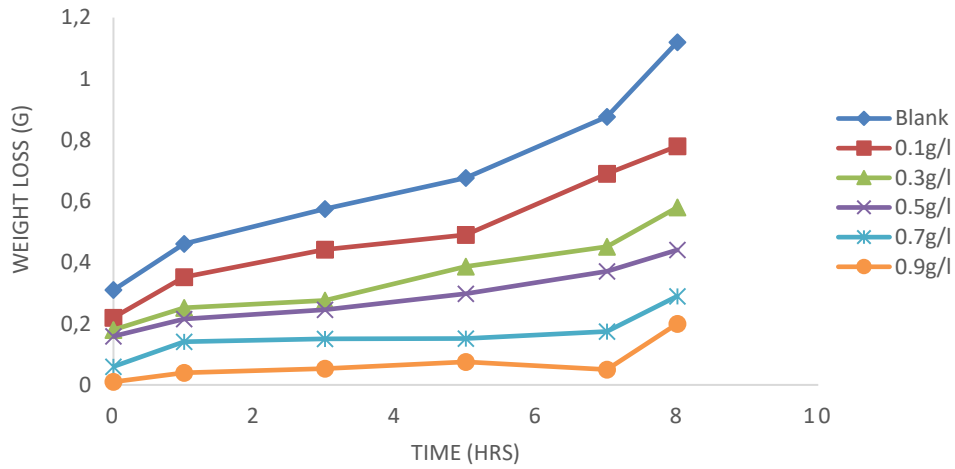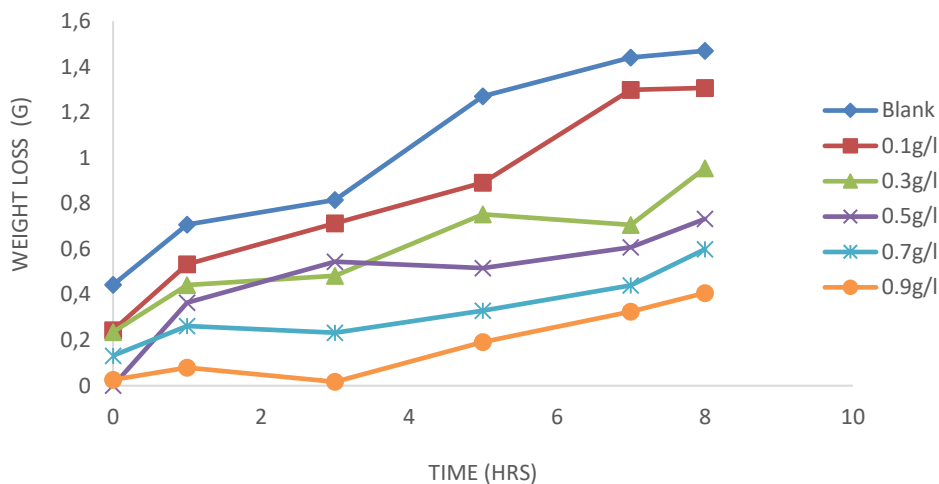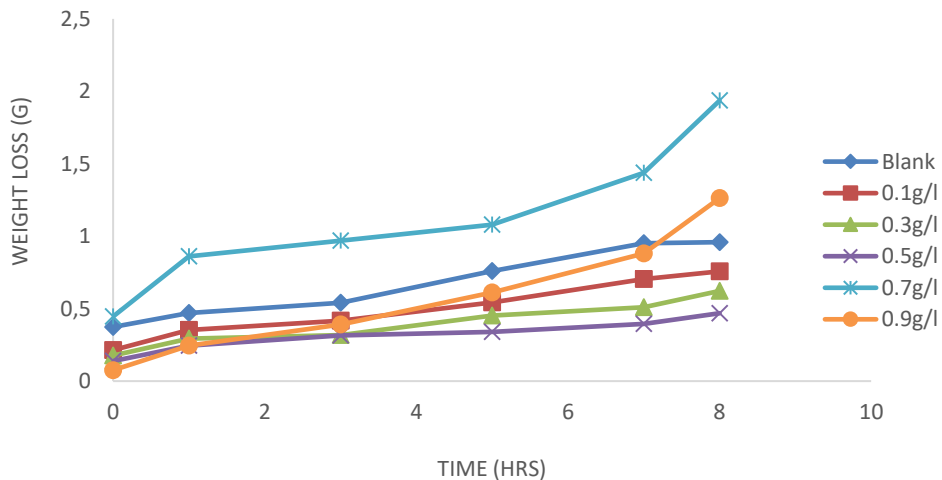
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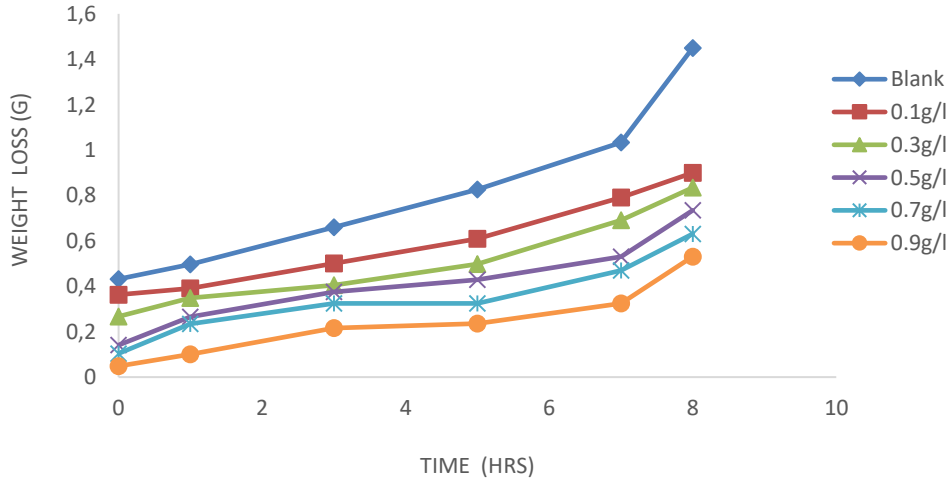
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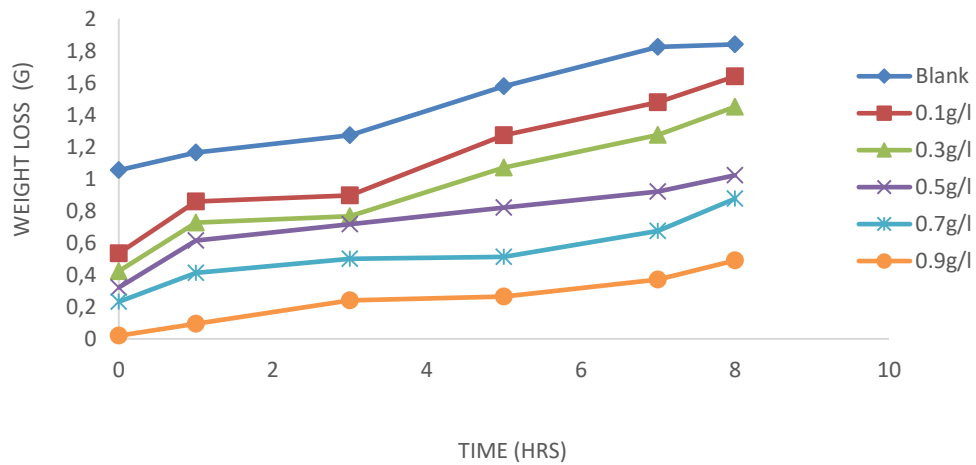
(c)

(d)

(e)

Figure 2. Effect of immersion on weight loss for aluminum in 0.1 % HCl; **(a)** AASS, **(b)** BESS, **(c)** DMSS, **(d)** MFSS, and **(e)** PMSS at 30 °C

3. 2. Thermometric considerations

The changes in temperature due to the corrosion process of Al in 2% HCl blank and inhibited solutions of different concentrations was carried out by way of employing the thermometric method, and presented in **Fig 3**. The plot of time against temperature in Fig. 3 shows that the dissolution of Al coupons did not proceed immediately after immersion at room temperature, but after some time had elapsed.

This elapsed time was necessary in order to overcome the 'incubation period' and as a result of the exothermic nature of the process, temperature increases progressively to a maximum, T_m. Additional increase in the concentration leads to a gradual decrease in the

maximum temperature (T_m) achieved, as shown in Figure 3. This can be attributed to adsorption of the different extracts on the Al surface, thereby blocking it from the aggressive acid environment. Similarly, curves of the same shape were obtained for other extracts at 30 ºC and 50 °C, respectively.

Reduction in reaction number (RN) of the system under consideration due to the decrease in maximum temperature (Tm) achieved within the shortest possible time is shown in **Figure 4**. It can be seen from the same Figure that an increase in concentration of shell extracts leads to decrease in RN and to inhibition efficiency, respectively.
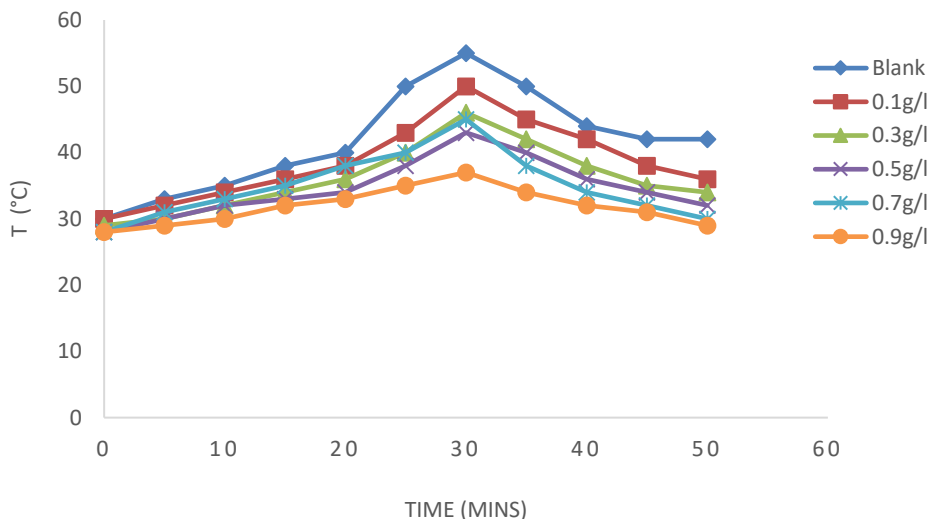
Figure 3. Temperature-time curves for aluminum corrosion in 2% HCl in the presence of different concentrations of AASS
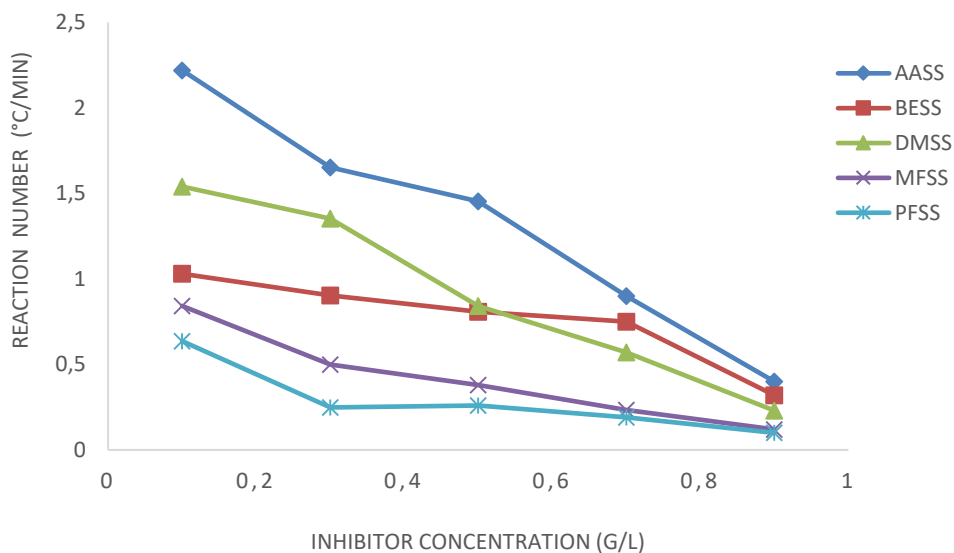
Figure 4. Plot of the reaction number (RN) against inhibitor concentration of different plant shell extracts

Table 1. Computed values of Corrosion rate, inhibition efficiency and surface coverage (θ) for Al in 0.1% HCl without and with different concentrations plant shell extracts at different temperatures

|	Inhibitor conc. (g/L)	Corrosion rate (g/cm²h)		Inhibition efficiency (%)		Surface coverage (θ)	
		30 °C	50 °C	30 °C	50 °C	30 °C	50 °C
	Blank	27.30	29.21	-	-	-	-
AASS	0.1	15.43	20.42	39.45	35.58	0.3945	0.3845
	0.3	15.11	17.78	45.04	59.87	0.4504	0.5987
	0.5	14.06	15.05	64.76	47.23	0.6476	0.4723
	0.7	10.20	12.14	75.03	74.89	0.7503	0.7489
	0.9	8.10	9.91	70.12	61.10	0.7012	0.6110
BESS	0.1	20.01	22.50	35.12	38.21	0.3512	0.3821
	0.3	11.91	14.33	70.54	59.01	0.7054	0.5901
	0.5	7.45	9.17	75.61	70.03	0.7561	0.7003
	0.7	5.03	6.83	76.75	79.87	0.7675	0.7977
	0.9	3.13	6.83	78.10	80.34	0.7810	0.8034
DMSS	0.1	16.32	18.90	51.21	42.13	0.5121	0.4213
	0.3	8.59	9.62	70.50	69.11	0.7050	0.6911
	0.5	3.45	5.86	78.69	70.52	0.7869	O.7052
	0.7	3.00	4.66	80.14	72.61	0.8014	0.7261
	0.9	2.81	2.81	82.31	82.31	0.8231	0.8231
MFSS	0.1	17.50	26.01	44.04	32.69	0.4404	0.3269
	0.3	10.11	21.25	61.83	76.19	0.6183	0.7619
	0.5	7.02	17.24	65.87	77.75	0.7787	0.4475
	0.7	6.10	13.49	78.27	67.27	0.7827	0.6727
	0.9	5.89	11.99	71.71	68.25	0.7171	0.6825
PFSS	0.1	23.15	22.45	36.32	34.75	0.3632	0.3475
	0.3	14.42	16.33	64.41	59.61	0.6441	0.5961
	0.5	9.17	10.67	77. 24	75.54	0.7724	0.7554
	0.7	6.83	8.83	79.31	60.14	0.7931	0.6014
	0.9	6.67	7.21	79.43	68.75	0.7943	0.6875

3. 3. Adsorption studies

The nature of metal-inhibitor interaction as regards the adsorption of a corrosion inhibitor can be better described using adsorption isotherms [4]. The degree of surface coverage (θ) presented in (Table 1) is important in the further discussion of adsorption isotherms. The degree of surface coverage data was obtained from the weight loss measurements using equation (6). The surface coverage values for AASS, BESS, DMSS, MFSS, and PFSS extracts were fitted into the Flory-Huggins and Langmuir adsorption isotherm model, which has the form (11) and (12); [27, 28].

❖ Flory-Huggins adsorption isotherm model, characterized by (10); [27]

$$log(\theta/_C) = \log K + xlog\,(1 - \theta) \tag{11}$$

where: 'x' is size ratio parameter, θ, is the degree of surface coverage, K is the adsorption equilibrium constant for the process, and C is the concentration of the inhibitor, and 'X' determines the magnitude of molecules adsorbed on the surface of the metal. A linear relationship was obtained from the graph of log (θ/C) against log (1−θ) of **Figure 5** for the corrosion inhibition of Aluminum studied at different temperatures, with R^2 almost equal to unity, as can be seen in **Table 2**. Similar plots were obtained for extracts at same temperature and 50 °C, respectively, but are not presented.
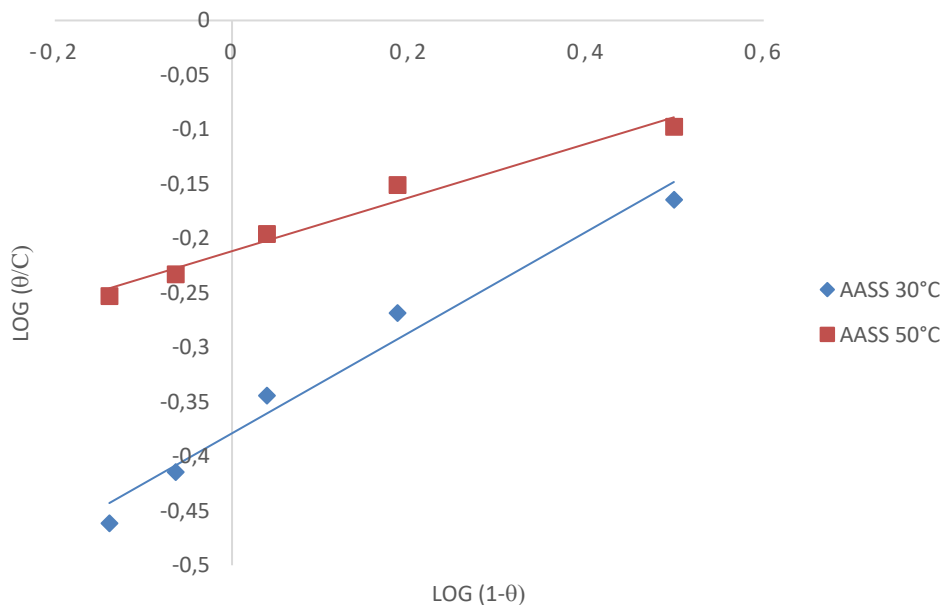
Figure 5. Flory-Huggins adsorption isotherm for aluminum corrosion in 1.0% HCl with AASS at 30 - 50 ºC

The positive values of 'x', as presented in Table 2 imply, that attraction (0 < x ≥ 1) exists between the size of molecules adsorbed on the surface of the metal, and that these are capable

of retarding the aggressive solutions from eating deep into the metal. It can be observed from the Table that the value of 'x' at 30 ℃ was higher than that at 50 °C, signifying that free energy of adsorption ($\triangle$G$_{ads}$) decreases as the temperature increases. This follows the Langmuir adsorption isotherm model, which has the form of (12); [28]:

$$KC = \frac{\theta}{1-\theta} \qquad (12)$$

The experimental data fitted in **Figure 6** reveal that log (C/θ) versus log C gave a straight line. This conforms with the Langmuir isotherm, signifying that the adsorption of the plant extracts obey Langmuir isotherm criteria. Also, it can be said that the standard free energy of adsorption ($\triangle$G°$_{ads}$) is related to the equilibrium constant (K) of the inhibitor constituents, and this was indicated by applying (13) [5, 29-30] and shown in Table 2:

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G°_{ads}}{RT}\right) \qquad (13)$$

Table 2. Results of adsorption parameters obtained from Flory-Huggins and Langmuir adsorption isotherm

Inhibitors	T (°C)	Flory-Huggins Isotherm					Langmuir Isotherm		
		R^2	K	$\triangle$G°$_{ads}$ (kJ/mol)	Isotherm value		R^2	K	$\triangle$G°$_{ads}$ (kJ/mol)
AASS	30	0.9983	0.1402	−5.1694	x	1.6673	0.9996	4.7854	−14.065
	50	0.9942	0.3125	−8.3763		0.6588	0.9677	0.3664	− 8.5438
BESS	30	0.9796	0.0742	−3.8303		1.8344	0.9929	0.0011	−7.0441
	50	0.9548	0.0607	−3.8921		0.3511	0.9543	0.0550	−2.9765
DMSS	30	1.0000	0.0268	−1.9219		1.5700	0.9156	0.0153	−0.4632
	50	0.9930	0.0003	−10.680		1.0341	0.9896	0.0045	−4.7893
MFSS	30	0.9886	1.0886	−20.345		1.2342	0.9919	1.1765	−10.4327
	50	0.9765	1.3842	−12.433		2.1322	0.9810	2.1126	−13.7692
PMSS	30	0.9953	0.2145	−15.326		0.6541	0.9987	0.4328	−17.2136
	50	0.9678	0.0673	−20.358		1.8766	0.9965	0.7654	−20.4321
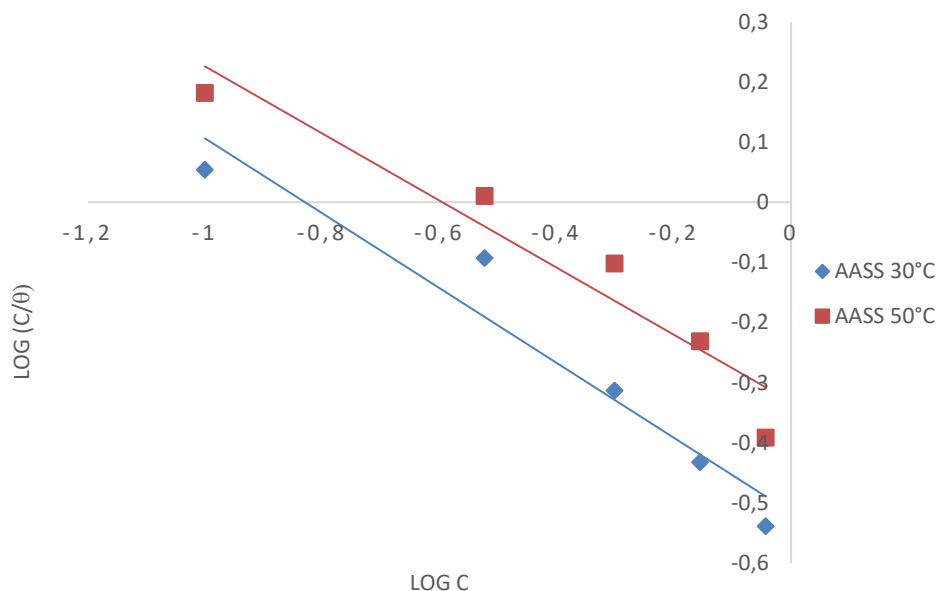
Figure 6. Langmuir adsorption isotherm for aluminum corrosion in 1.0% HCl
with AASS at 30 - 50 ºC

In Table 2, R is the universal constant, T is the absolute temperature and 55.5 is the concentration of water molecules in mol/L. The equilibrium constant K usually signifies the strength between adsorbate and adsorbent [5]. Hence, high K values will amount to extra effective adsorption and improved inhibition efficiency. Therefore, in this study, MFSS extract with greater K values (in both isotherms) at all temperatures is considered a better inhibitor when compared to AASS, BESS, DMSS, and PFSS extracts.

Moreover, in Table 2, all the values of $\triangle G°_{ads}$ were negative. This implies that the extracts were adsorbed on the Al surface spontaneously. Furthermore, it can be deduced from the negative values of $\triangle G°_{ads}$ in all cases that the two adsorption isotherms studied are comparable. That the calculated values of ΔG_{ads} are less and equal to –20 kJ/mol shows that the shell extracts were adsorbed on the Al surface by physical processes [31].

3. 4. Effect of temperature

The inhibition action of AASS, BESS, DMSS, MFSS, and PFSS was studied at two different temperatures (30 and 50 °C), using weight and thermometric measurements. The results presented in Table 1 show that an increase in temperature causes significant increase in the CR. This is probably due to the desorption of adsorbed shell extracts molecules from the Al surface at high temperatures [31]. However, inhibition efficiency of the shell extracts decreases with temperature rise as seen in the same Table 1. This result indicates that physical adsorption of the inhibitor molecules occurred on the Al surface. The effect of temperature can be clearly established using Arrhenius and transition state equations (Eqs. 14 and 15) [31-32]:

$$CR = A \, exp\left(-\frac{E_a}{RT}\right) \tag{14}$$

$$CR = \frac{RT}{hN} exp\left(\frac{\Delta S^\circ}{R}\right) exp\left(-\frac{\Delta H^\circ}{RT}\right) \qquad (15)$$

where: A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, T is the absolute temperature, ΔS° is the entropy of activation, ΔH° is the enthalpy, N is the Avogadro number, h is the Planck constant. The Arrhenius plot of logarithm of CR with reciprocal of absolute temperature (**Figure 7a**) gives a straight line from which the Ea values were evaluated (**Table 3**). The plot of log (CR/T) versus 1/T as shown in Figure 7**b** gives a straight line with a slope of $(-\Delta H^\circ/2.303\ R)$ and an intercept of log (R/Nh + $\Delta S^\circ/2.303\ R$) from which the values of ΔH° and ΔS° were deduced and listed in Table 3.

Table 3. Kinetic and thermodynamic parameters obtained from Arrhenius and transition state plots

	Inhibitor conc. (g/L)	Ea (kJ/mol)	△H° (kJ/mol)	△S° (J/mol/K)
	Blank	63.4	58.2	−55.6
AASS	0.1	65.1	59.7	−46.9
	0.3	67.5	63.3	−45.8
	0.5	69.2	65.6	−40.9
	0.7	70.0	66.7	−45.8
	0.9	71.1	68.4	−52.4
BESS	0.1	41.3	39.7	−21.6
	0.3	47.5	40.4	−24.0
	0.5	48.2	42.6	−25.7
	0.7	49.1	46.3	−26.4
	0.9	51.3	50.8	−28.4
DMSS	0.1	53.1	51.3	−74.2
	0.3	56.5	54.3	−75.0
	0.5	56.6	55.5	−76.2
	0.7	60.2	56.9	−78.1
	0.9	67.8	54.2	−79.5
MFSS	0.1	62.7	58.4	−46.0
	0.3	55.6	54.3	−53.9
	0.5	51.4	50.1	−54.8
	0.7	50.0	49.0	−57.5

	0.9	49.4	45.4	−60.3
PMSS	0.1	64.3	58.8	-66.4
	0.3	65.4	61.3	−68.5
	0.5	71.1	68.5	−70.1
	0.7	72.7	69.9	−73.2
	0.9	75.6	70.7	−71.9
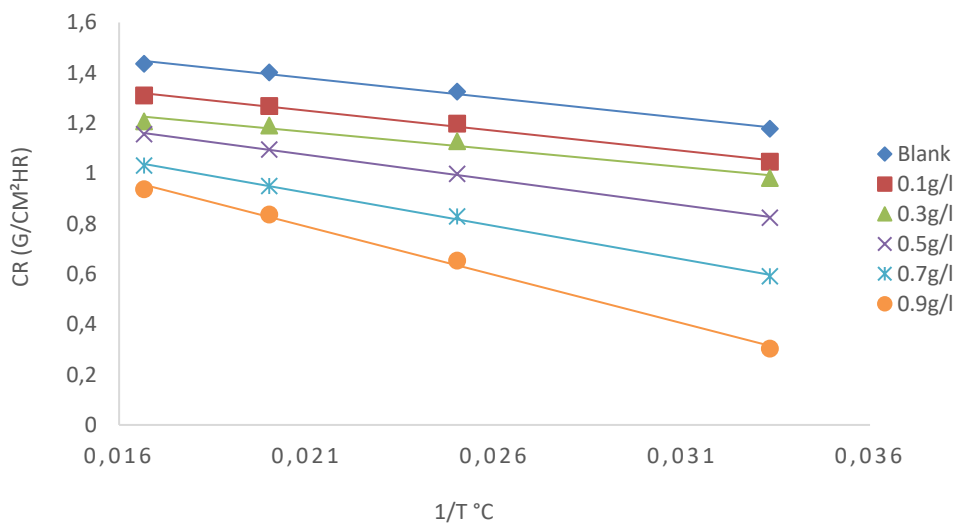
Figure 7a. Arrhenius plots of log CR against 1/T for Al in HCl and that inhibited by different concentrations of AASS
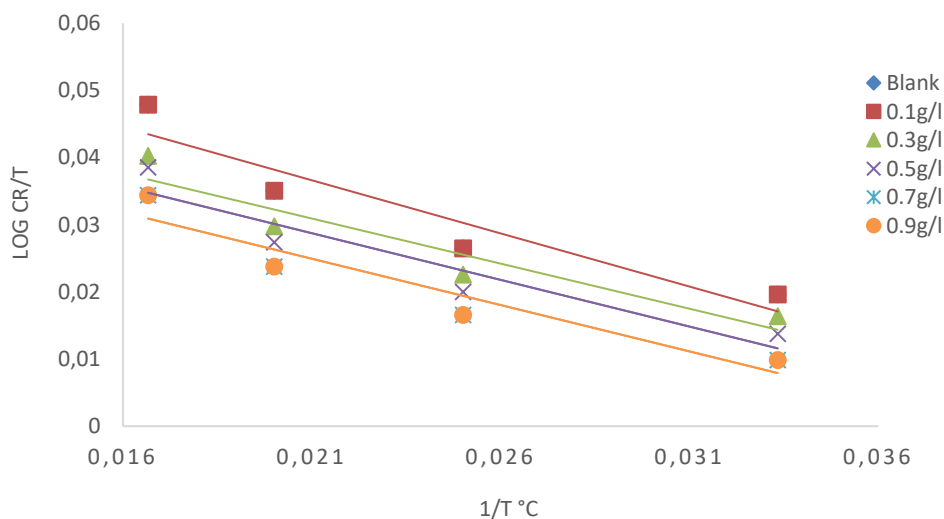
Figure 7b. Transition state plot of log CR/T against 1/T for Al in HCl and that inhibited by different concentrations of AASS

The positive values of ΔH° imply an endothermic reaction and slow dissolution of the Al, while, on the other hand, the negative values of △S° indicate a decrease in disordering proceeding from the reactants to the activated complex. Similar plots of Arrhenius and Transition state plots were generated for inhibitors (not presented).

4. CONCLUSIONS

AASS, BESS, DMSS, MFSS, and PMSS were evaluated as inhibitors for Al corrosion in 2.0% HCl. The study discloses that the inhibitors are efficient and effective corrosion inhibitors with a better inhibition efficiency at all temperatures. The inhibition efficiency increases as the concentration of the extracts increases and follows the order DMSS > BESS > AASS > MFSS > PFSS. The shell extracts retard the corrosion of Al by forming a protective oxide film that was physically adsorbed on the metal surface. The adsorption phenomena follow Flory-Huggins and Langmuir isotherms.

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