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Corrosion Inhibition Potential of *Lagenaria breviflora* (Christmas melon) Leaf Extract on Aluminium in Hydrochloric Acid Environment

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ABSTRACT: The objective of this paper was to investigate the corrosion inhibition potential of *Lageneria breviflora* (Christmas melon) leaf extract (LELB) on aluminium in 0.5M hydrochloric acid environment using weight loss method. Data obtained from phytochemical constituents LELB reveals the presence of tannins, diterpenes, sterols, flavonoids, cardiac glycosides, and phenols. FT-IR analysis indicates O-H and N-H stretching vibrations identified in the 3193.73 cm^{-1} range and S-C=N stretching vibrations in the 2163.89 to 2114.61cm^{-1} range. The C-N bond stretching vibration was observed around 1243.19 cm-^{1,} whereas the N-H bond vibration was noted at about 1592.20 cm^{-1}. The C-I functional group was assigned the absorption bands seen at 523 cm^{-1}. Weight loss analysis indicates that LELB extract had 68% corrosion inhibition efficiency for aluminium in 0.5M hydrochloric acid environment. Thermodynamic parameters and activation energy were also evaluated. Fourier transform infrared spectroscopy (FTIR) analysis confirmed the formation of an adsorbed protective film on the aluminium surface. The findings suggest that *lagenaria breviflora* leaf extract could be an effective corrosion inhibitor for aluminium in hydrochloric acid solutions.

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Extensive research has been conducted on the corrosion resistance of aluminium and its alloys in various environments due to their prevalence. These studies often focus on the properties of the naturally formed or iodized surface oxide film. However, aluminium remains susceptible to corrosion in aqueous acidic conditions. Acidic solutions are commonly used in industrial processes such as cleaning, descaling, and pickling of metals, which can lead to significant metal dissolution (Olasunkanmi and Ebenso 2020). Additionally, metals exposed to aggressive environments experience severe corrosion attacks. The use of corrosion inhibitors during acid pickling is a practical approach to mitigating metal degradation in acidic media. Organic compounds have long been recognized as effective corrosion inhibitors, primarily acting through adsorption onto the metal surface

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(Iroha*et al.,* 2005). Metals provide enhanced protection against active corrosion sites when adsorption occurs via heteroatoms such as sulphur, nitrogen, oxygen, phosphorus, or through triple bonds or aromatic rings.

However, some conventional corrosion inhibitors are both costly and pose environmental hazards (Iroha and Akaranta 2020). Green corrosion inhibitors, derived from natural chemicals, provide a sustainable, biodegradable, and eco-friendly alternative. Although there is evidence suggesting that plant extracts may prevent corrosion, current research has focused on the use of plant-derived inhibitors for metal protection, a practice that has existed since the late 19th century (Palimi *et al.*, 2023). These extracts contain various hydroxyl-rich organic compounds, including tannins, phenol, flavonoids, cardiac glycoside, sterols, and alkaloids as well as nitrogen-containing compounds, which contribute to their inhibitory properties. Leaf extract of*lagenaria breviflora*(LELB) is a perennial plant from the Cucurbitaceae family. It is a perennial climber ascending to the forest growing canopy, occurring from Senegal to West Cameroons and generally widespread in tropical Africa (Oridupa *et al.*, 2011).

Researchers have identified triterpenoids, saponins, phenols, alkaloids, anthraquinones, flavonoids, tannins, and carotenoids in the plant via phytochemical examinations. These investigations have been conducted by (Elujoba *et al.*, 1990; Banjo *et al.*, 2013; Adeyemi *et al.*, 2017).). Flavonoids and tannins, commonly present in plant extracts, are known for their ability to reduce the corrosion rate of metals and alloys in aggressive environments (James andIroha 2019). The objective of this paper is to investigate the corrosion inhibition potential of *lageneria breviflora* (Christmas melon) leaf extract (LELB) on aluminium in 0.5M hydrochloric acid environment using weight loss method.

MATERIALS AND METHODS

In this study, aluminum coupons of 2 cm x 3 cm x 2 mm were used in weight loss study, they were polished with fine-grade emery sheets, air-dried, and then cooled in a desiccator. : Elemental composition of aluminium alloy employed for the studywere analyzed. Table 1 shows the composition of aluminum.

Table 1: Composition of aluminium metal in weight %

Element	Al	Mg	Fe	Cu	Zn	Cr	Ti
% Wt.	**97.20**	**0.902**	**0.702**	**0.210**	**0.022**	**0.265**	**0.312**

Preparation of plant extract and the inhibitor solution: Leaf extract of (Christmas melon) *lagenariabreviflora* (LELB) plant was collected, from Igwuruta-Ali inIkwere Local Government Area, Rivers State, air dried for 10 days and grinded using a manual blender, weighed and stored in an air tight container. 100 g of crushed LELB were immersed in 1 litre of ethanol for 7 days to get the plant extract. The mixture were first sieve with muslin cloth, the liquid obtained were subsequently filtered using whatman No 1 filter paper, the filtrate was then concentrated using a water bath until a solid residue was obtained at 78°C. The yield of plant extract was found to be 5.94%. The concentration range of inhibitor used was from 0.1 to 0.5 g/L. The phytochemical in the extract were determined using the method reported by (Tiwari et *al.*, 2017).

To determine the weight loss, metal coupons were immersed in a 100 ml beaker containing 0.5M HCl with varying concentrations of an inhibitor. The test was conducted at temperatures of 303 K, 313 K, and 323 K for a period of 1 hour. The coupons were taken out from the water, washed under running water, and then dried and cooled in a desiccator after immersion. The weight of the metal coupon was measured both before and after immersion. Difference in weight loss and the inhibition efficiency (IE) of the inhibitor were calculated using the following formula:

$$\text{IE}\ (\%) = \frac{W0 - W1}{W0} * 100 \quad (1)$$

Where IE = Inhibition efficiency, W_0 is the initial weight of coupon uninhibited (blank) and W_1 is the final weight of the coupon in uninhibited acid medium.

The weight loss of the aluminium coupon was determined using the equation (2),

$$\text{Weight loss}\ \Delta\text{W (g)} = Wi - Wf\ (2)$$

Where, W_i is the initial weight of aluminum coupon before immersion, while W_f is the final weight of aluminum coupon after immersion.

Thermodynamics Parameters: The equations (3, 4) for the parameters. The corrosion rate is presented in equation 3.

$$\log C_R = \log A - \frac{Ea}{2.303RT} \quad (3)$$

Where, C_R is the corrosion rate at temperature T, R is the universal gas constant (8.314 $Jmol^{-1}$ K^{-1}) and Ea is the activation energy of the process.

The apparent enthalpy of activation (ΔH_{ads}) and apparent entropy of activation (ΔS^*) could be obtained be re-arranging equation 4

$$C_R = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \quad (4)$$

Where, N is the Avogadro's number, h is the Planck's constant, ΔH^* is the apparent activation enthalpy and ΔS^* is the apparent entropy of activation.

Free energy of adsorption (ΔG_{ads}) were calculated using the equation (5),

$$\Delta Gads = -2.303\ RT\log(55.5Kads) \quad (5)$$

Where 55.5 is the standard molar of water in solution, K is the equilibrium constant of adsorption.

RESULTS AND DISCUSSION

Phytochemical analysis: Table 2 presents the phytochemical constituents of the ethanol extract of (LELB). The results confirm the existence of tannins, diterpenes, sterols, flavonoids, cardiac glycosides, and phenols in LELB. The presence of heteroatoms in these organic compounds may improve metal corrosion inhibition under acidic conditions. It has been revealed that the presence of these compounds promote the corrosion inhibition of aluminium in aggressive acid media, as it agrees with the work of (Iroha andMaduelosi2021). It also an evidence that the inhibition efficiency of the extract is as a result of the presence of the phytochemical constituents (Odiongenyi *et al*., 2009; Nwabanne *et al*., 2012).

Table 2: Phytochemical composition of LELB

Phytochemical	Leaf Extract
Flavonoids	++ve
Tannins	+ve
Diterpenes	+ve
Cardiac Glycosides	+ve
Sterols	+ve
Phenol	+ve

++ Abundance, + Presence

Infrared spectra analysis: The functional groups in *Lagenaria breviflora* leaf extract (LELB) were characterized using Fourier transform infrared spectroscopy. Figure 1 illustrates the findings of the FT-IR analysis, indicating the existence of many functional groupings. Absorption bands corresponding to O-H and N-H stretching vibrations were identified in the 3193.73 cm^{-1} range, whereas bands related to S-C=N stretching vibrations were seen in the 2163.89 to 2114.61 cm^{-1} range. The C-N bond stretching vibration was observed around 1243.19 cm^{-1}, whereas the N-H bond vibration was noted at about 1592.20 cm^{-1}. The C-I functional group was assigned the absorption bands seen at 523 cm^{-1}. The phytochemical results align with the functional groups present in LELB extracts. The corrosion inhibition characteristics of LELB are attributed to the presence of aromatic and amine functional groups in the leaf extract of *lagenaria breviflora* (Okewale and Adesina2021).

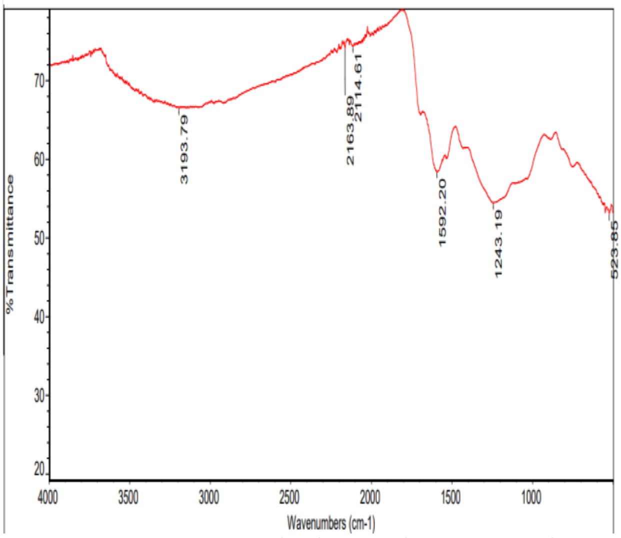

Fig.1: FTIR Spectroscopy of leaf extract of *lagenaria breviflora*

Weight loss analysis: The findings of this study indicate that LELB extract can be used as corrosion inhibitor. The highest inhibition efficiency exhibited by LELB is 68%. Figure 2 demonstrates this. It is speculated that inhibition efficiency could be a function of chemical bond formation between the inhibitor and the aluminium.

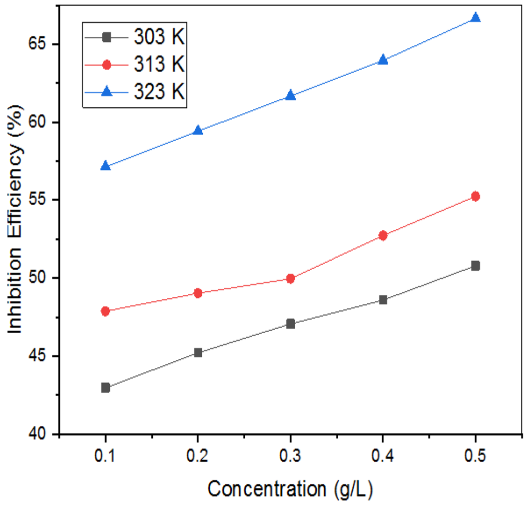

Fig.2: Variation of inhibition efficiency with concentration of LELB inhibitor for Al corrosion in 0.5M HCl at different temperatures.

Furthermore, the low result in inhibition efficiency can be attributed to the absence of important phytochemical in the extract.The adsorption of inhibitor molecules onto the aluminum surface typically represents the first phase in a corrosion inhibition process. Factors to consider include the aggressive electrolyte type, the chemical structure of the inhibitor molecule, the nature and charge of the metal, and the adsorption process (Mathina and Rajalakshmi, 2016).

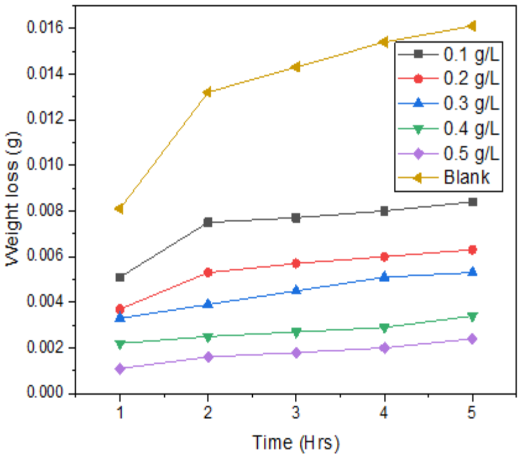

Fig.3: Variation of weight loss with time of Al in 0.5 M HClat 303 K in the presence and absence of different concentration of LELB.

At temperatures of 303K, 313K, and 323 K, the weight loss of aluminum was determined using equation 2 at various inhibitor concentrations, as seen in Figures 3 to5. The presence of the inhibitor significantly reduces the weight loss of the metal coupons compared to its absence. The findings indicate that variations in inhibitor concentration and immersion duration resulted in reduced weight loss of the coupons (Louis *et al*., 2016).

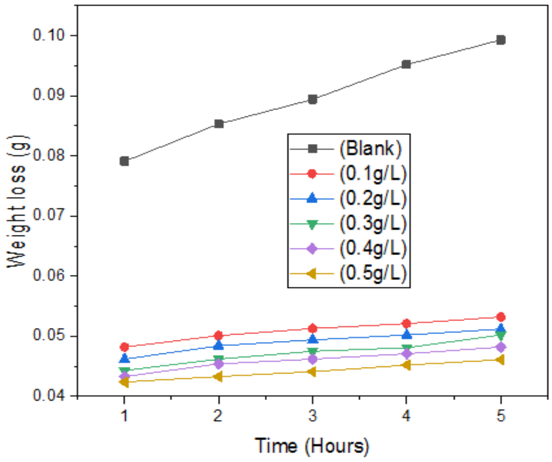

Fig.4: Variation of weight loss with time of Al in 0.5 M HCl at 313 K in the presence and absence of different concentration of LELB.

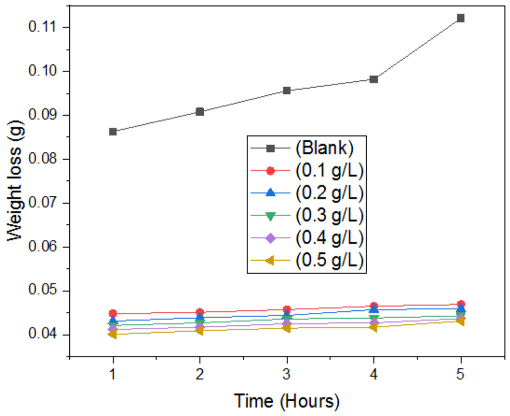

Fig.5: Variation of weight loss with time of Al in 0.5 M HClat 323 K in the presence and absence of different concentration of LELB.

Thermodynamic analysis: plot of log (CR/T) against 1/T is seen to be linear in Figure 6 from which (ΔHo) and (ΔSo) values were deduced from the slopes and intercept of the graph respectively and listed in table 3, equation(4). Arrhenius equation represented by equation (3) was used to calculate the activation energy (Ea) in the presence and absence of *lageneria breviflora* leaf extract inhibitor. Lower Ea value in the presence of inhibitors in comparison to the blank is attributed to chemical adsorption (Umoren *et al*., 2010; Thirumoolan *et al*., 2014). Higher activation

(Ea) in the presence of inhibitor compared to the blank can be attributed to physical adsorption mechanism. In this study, the decreasing values of activation Ea clearly showed a chemical adsorption of inhibitor molecules on aluminium surface. The positive sign of the enthalpy of activation as obtained in the present study shown in Tables 3 shows the endothermic nature of the process of aluminium dissolution. The enthalpy of activation (ΔHo) values in the presence and absence of inhibitor are positive, close and exhibited the same trend noticed in Ea. From literature, the negative sign of (ΔH_{ads}) has been clearly associated with an exothermic adsorption process that can either be physisorption or chemisorption or combination of both. However, the positive sign is connected to endothermic adsorption (Okewale and Adesina, 2020).The activation entropy (ΔS_{ads}) in the absence and presence of LELB extract inhibitor was positive. This can be interpreted to mean that organic molecules were orderly adsorbed on the surface of the metal.

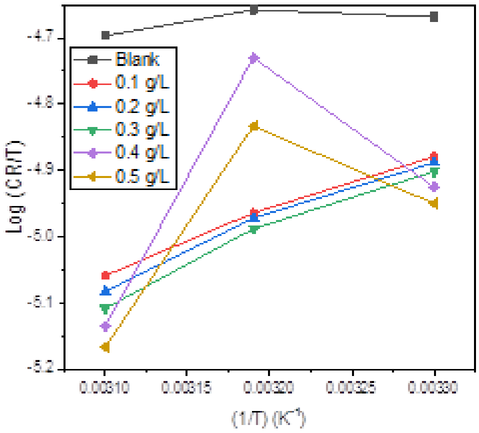

Fig.6: Transition state plot of Al in 0.5M HCl in LELB

Table 3: Corrosion activation parameters for Aluminium LELB in 0.5M HCl in the absence and presence of different concentrations of inhibitors

Inhibitor	**Concentration (g/L)**	**E_a (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol/K)**
	Blank	72.685	71.948	-57.294
LELB/	0.1	64.628	61.983	--96.139
HCL	0.2	60.519	57.874	-112.39
	0.3	59.858	57.203	-133.12
	0.4	59.129	56.378	-115.02

Adsorption isotherm analysis: Freudlich isotherm was used to model the adsorption of LELB on to the aluminium surfaces. The isotherm parameters were shown in Table 4 and the plot in Figure 7. The value of correlation coefficient (R^2) was used to determine the best fit. Freundlich adsorption isotherm model was found to be the best fit for the adsorption of the inhibitors on aluminium. The free energy of adsorption, ΔGads, was calculated using equation (5). Negative ΔGads values for inhibitor adsorption on metal surfaces imply a spontaneous process, while positive values signify non-spontaneous processes, as noted by Fouda *et al.*, 2009; Shukla and Ebenso 2011).

Surface morphology analysis: SEM surface examination was conducted on the aluminum surface with and without LELB extract. The results are shown in Figure 8. The aluminium specimen's surface retrieved from the 0.5 M HCl solution without inhibitor (Figure 8a) shows a rough surface with evidence of corrosion damage as pits and cracks. However, the aluminium specimen's surface retrieved from the acid solution containing LELB extract inhibitor (Figure 8b) shows flower like shapes of LELB inhibitor covering the surface of the metal. The added LELB extract covered almost all the openings present on the surface, forming a barrier between the metal and the acid medium, preventing more corrosion from taking place.

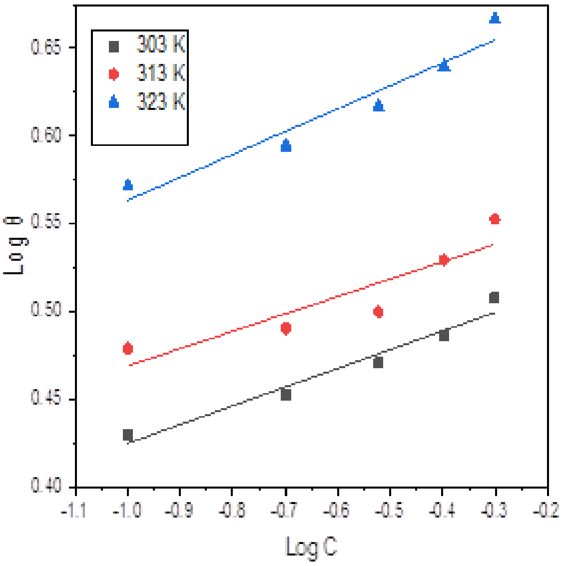

Fig.7: Isotherm graph/ Freundlich LELB aluminium HCl

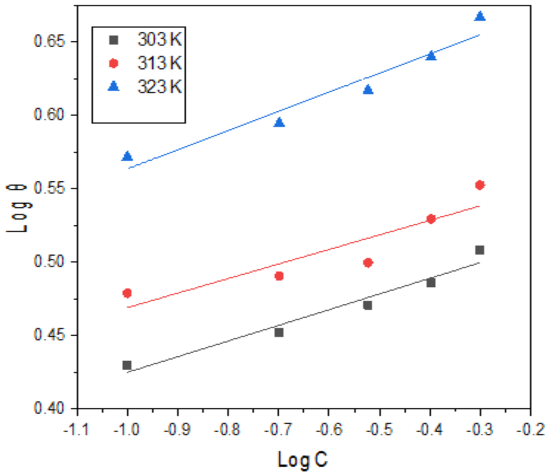

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Table 4: Freundlich isotherm for adsorption of inhibitors on aluminium surface

Inhibitor/ Acid Media	**Temp (K)**	**R^2**	**Slope**	**Intercept**	**K_{ads}**	**ΔG (kJ/mol)**
LELB/HCl	303	0.9763	0.2680	0.6977	4.9853	-14.167
	313	0.9932	0.1322	0.5528	3.5710	-13.766
	323	0.9724	0.2629	0.8105	6.4639	-15.800

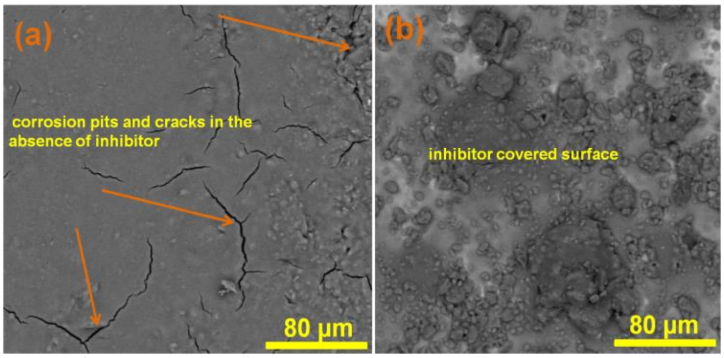

Fig.8: SEM images of the morphology of (a) uninhibited and (b) LELB inhibited aluminium surface in HCl.

*Conclusion***:** The presence of phytochemical molecules in the leaf extract of*lagenariabreviflora* makes it a prospective alternative to synthetic corrosion inhibitor for aluminium in hydrochloric acid environment;it is safer andwill reduce the cost of corrosion control.This study further shows that the inhibitor is of multilayer, chemically absorbed on the surface of the metal. Future improvements may include development of modified corrosion inhibitors possessing excellent adsorption ability to attain more attractive anticorrosion performance.

Declaration of Conflict of Interest: The authors declare no conflict of interest

Data Availability Statement: Data are available upon request from the first author or corresponding author or any of the other authors

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