

Comparison of Selected Plant Extracts As Green Corrosion Inhibitors for Aluminium in 1.0 M HCL Solution

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Abstract: The inhibitory effect of Leaf Extracts of utazi (*Gongronemalatifolium*) (LEGL), eggplant (*Solanum melongena*) (LESM), vegetable fern (*Athyrium esculentum*) (LEAE) and Oji-awusa (*Cola acuminata*) (LECA) on the corrosion of aluminium in 1.0 M HCl were investigated at the following temperatures: 30°C, 40°C, and 50°C. The experiment was carried out with same concentrations of the above extracts using weight loss method. Some key performance indicators such as percentage inhibition efficiency (IE%), Corrosion rate (CR) and the adsorption properties at different temperatures were monitored and compared. The trend of the percentage inhibition efficiency obtained showed that LECA > LEAE > LEGL > LESM at 50%v/v concentration, and LESM > LEGL > LEAE > LECA at 30°C, LEAE > LESM > LECA > LEGL at 40°C, and LECA > LEAE > LEGL > LESM at 50°C, showing the variation in effectiveness of these inhibitors and their resistance to adverse conditions such as high temperature and environmental factors. The corrosion rate (CR) and adsorption properties of LECA further confirmed its performance and resistance to adverse conditions which could be the bases for its most effective performance as a protection for aluminium among the four inhibitors.

Keywords: Comparison, Extracts, Corrosion Inhibition, Aluminium

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I. Introduction

Comparison of corrosion inhibitors was aimed at experimentally determining a suitable inhibitor for the corrosion of aluminium. This became imperative as different inhibitors inhibit corrosion differently on different metals in the presence of adverse conditions such as temperature and micro-organisms [1].

Extracts from plants which is the focus of researchers today as green corrosion inhibitors contains a large number of organic compounds [2]. Notable among these are: tannin, saponin, pregnane, alkaloids, flavonoids, glycosides, phytosterol etc. These organic compounds are rich in heteroatoms such as; phosphorus, nitrogen, sulphur and oxygen [3]. Heteroatoms are electron rich organic compounds and therefore, very good for corrosion prevention with the advantage of being environmentally friendly and biodegradable over inorganic inhibitors such as hydrazine etc. which are poisonous and thus environmentally unacceptable.

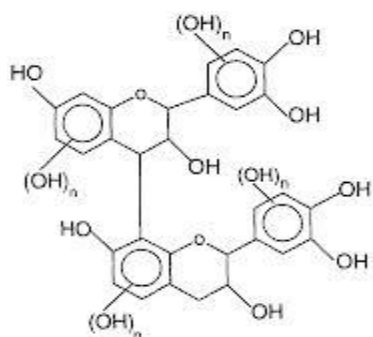
Corrosion is a destructive chemical reaction on metals and other materials. It occurs due to the presence of acid, water molecules and oxygen from the air [4]. This causes a tremendous damage to industrial metals such as iron (carbon steel or mild steel) and aluminium.

Aluminium is a remarkable metal that has low density and corrosion resistance due to ability of the metal to go into passivation. But the corrosion resistance is reduced by environments such as aqueous salts, presence of dissimilar metals and acidic solution. Aluminium corrodes by losing three electrons and going into solution as a positive ion, that is Al^{3+} .

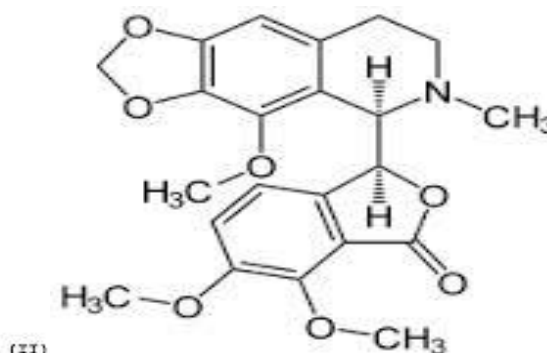
$Al \rightarrow 3e^- + Al^{3+}$ in the presence of acid. Similar results were obtained by other researchers such as [5], [6] and [7]. Aluminium is one of the few metals that retain silvery reflectance in finely powdered form, making it an important component of silver coloured paints. Therefore, aluminium corrosion inhibition using natural extracts is of great economic importance.

Several authors have reported the use of different leaf extracts as corrosion inhibitors, notable among them include the corrosion inhibition behavior of three plant extracts on mild steel: okazi leaf (*Gnetum africanum*), utazi leaf (*Gongronemalatifolium*) and Elizabeth leaf (*Chromolaena odoratum*), the result showed that Elizabeth leaf was the best among the three, it had the highest inhibition efficiency, [8]. Researchers have made so many attempts on search for a suitable extract for corrosion control of different metals. Plant extracts like aqueous extract of fenugreek leaves was long ago investigated by [9], aqueous extract of olives leaf (*Olea europaea*) [10].

The ability of natural extracts to inhibit corrosion of aluminium is investigated in the present research with a focus on comparing the effects of adverse conditions on inhibitors using the following plant extracts: *Gongronemalatifolium* (LEGL), *Solanummelongena* (LESM), *Athyriumesculentum* (LEAE) and *Cola acuminata* (LECA). From the proximate analysis it was discovered that these plant extracts contain electron rich compounds in different proportions [11]. The compounds such as ; tannin, alkaloids etc. as mentioned earlier are structurally shown below; scheme 1 and 2. They are capable of inhibiting corrosion of metals to a large extend and are contained in these extracts, [12].



Scheme 1 Tannin



Scheme 2 Alkaloids

II. Experimental

2.1 Sample collection

Fresh leaves of Utazi (*Gongronemalatifolium*), Eggplant (*Solanummelongena*), Vegetable Fern (*Athyriumesculentum*) and Oji-awusa (*Cola acuminata*) were obtained from Kpor community, Gokana Local Government Area of Rivers State, Nigeria.

2.2 Preparation of leave extract

The leaves of *Athyriumesculentum* were sun dried for three days and ground properly to powder, from which 54.19 g were weighed and soaked with 500 ml of ethanol, shaken properly and allowed to stand for 7 days. Ethanol volume was regularly checked within this period with more ethanol added to maintain the ethanol level. Resultant solution was filtered and more volume of ethanol was added and allowed to stand for one hour. After which it was filtered again, more volume of ethanol added continuously until the required volume of the leaf extract was obtained, the total volume of ethanol used was 1200 ml. This was used as the stock solution from which 10% v/v, 20% v/v, 30% v/v, 40% v/v, and 50% v/v concentrations of the inhibitor were prepared. The same process was used to prepare the other three leaves; *Gongronemalatifolium*, *Solanummelongena* and *Cola acuminata* leaves.

2.3 Preparation of the Aluminium Coupons

Aluminium specimens used in this experiment was cut into dimensions: 4.0 cm x 4.0 cm x 0.01 cm. A perforation of about 2 mm in diameter was made near the upper edge to allow passage of rubber thread for suspension and easy removal of the metals in and out of acid solution. The specimens of aluminium sheet were thoroughly cleaned, buffed and rubbed with emery paper to obtain a mirror-like spotless surface. It was washed with iron sponge in absolute ethanol, degreased by rinsing in acetone, dried and stored in a desiccator to prevent contact with moisture before use.

2.4 Weight loss determination

The aluminium coupons kept in the desiccator were carefully weighed. Each coupon was placed into a 100 ml beaker container containing the same concentration of the four inhibitors. This was done with the aid of rubber thread and was allowed for 30 minutes after which it was retrieved washed, dried, reweighed, and placed back into the test solution for the next 30 minutes. The experiment was carried out with different concentrations of the inhibitors from 10%, 20%, 30%,

40% to 50% v/v for replicate values at the temperature of 30°C and repeated at temperatures of 40°C and 50°C. The temperature was regulated using a thermostatic water bath and the results were recorded and analyzed accordingly. The inhibition efficiency and surface coverage (θ) were calculated using

$$\% \text{ Inhibition Efficiency} = \frac{\Delta W_b - \Delta W_i}{\Delta W_b} \times 100 \dots (1) \text{ and } \theta = \frac{\Delta W_b - \Delta W_i}{\Delta W_b} \dots (2) \text{ respectively.}$$

Where; ΔW_b and ΔW_i are the weight loss of aluminium coupons in the blank and in the solution containing inhibitors respectively as previously used and reported by [7], [6].

III. Results and Discussion

3.1 Corrosion rate and the percentage inhibition efficiency

The evolution of hydrogen gas and gradual mass loss observed as the aluminium metal coupons were periodically removed and weighed were indicative of the fact that aluminium corrodes in 1M HCl. While the gradual reduction in corrosion rate as observed in all the systems containing inhibitors, LEGL, LEAE, LESM and LECA showed that the four inhibitors actually inhibited the corrosion of aluminium in 1M HCl with LECA showing the highest reduction in corrosion rate, (Figure 1). This could be explained as the ability of these inhibitors to adsorb on the surface of the metal, forming an interface that separated the metal from the acid, water and air. This observation could be supported by the increasing percentage inhibition efficiency as the concentrations of the inhibitors were increased [13], (Figure 2). It was also observed that the four inhibitors were similar or very close in their percentage inhibition efficiency (IE%) at ambient temperature, all attaining percentage inhibition efficiency above 90% at concentrations of inhibitors between 40 – 50% v/v.

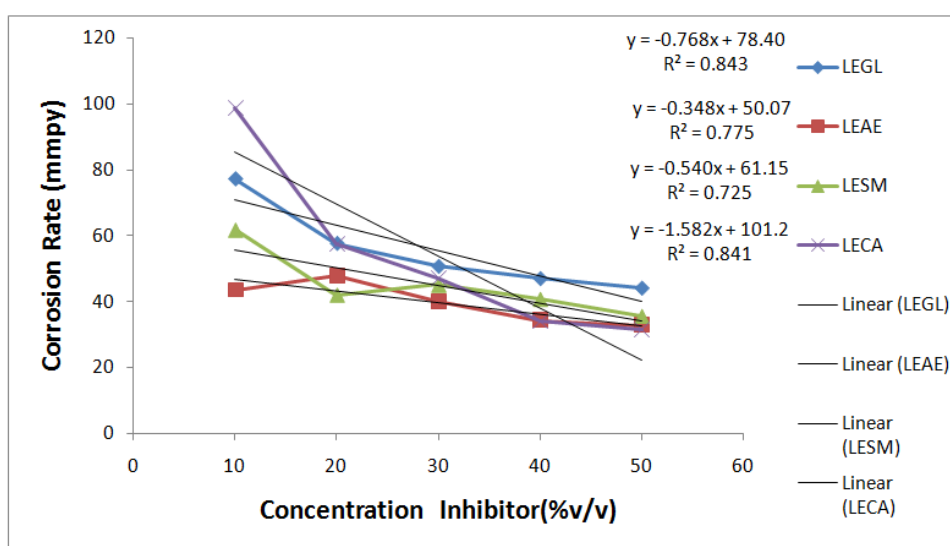


Figure 1 corrosion rate of aluminium against inhibitor concentrations in 1M HCl for the different inhibitors

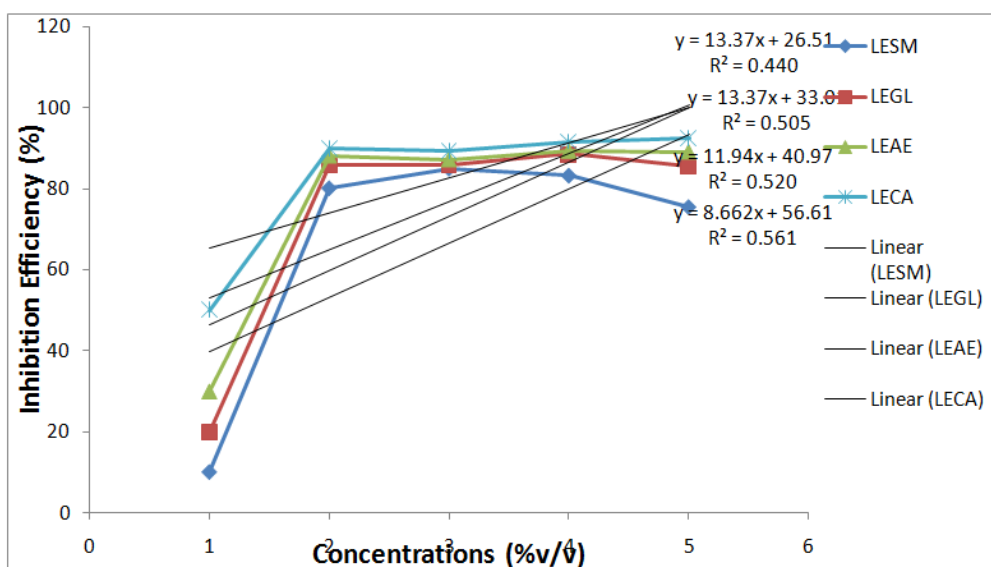


Figure 2 Inhibition efficiency against concentrations of the different inhibitors plotted.

3.2 Effects of Temperature on Corrosion rate

However, there was reduction in the percentage inhibition efficiencies of the inhibitors as the temperature of the reaction system increased from 30°C to 50°C, (Figure 3). This is in line with the reports of previous authors who reported that inhibition efficiency decreases with increase in temperature [14]. This could be as a result of desorption or weak adsorption of these inhibitors on the metal surface at this temperature [15], Figure 4. Effects of temperature on corrosion reactions could be explained from the fact that temperature rise increases the rate of the following parameters: desorption of inhibitor molecules, kinetic energy of both the inhibitor and the corrosive molecules, solubility of the adsorption film, decomposition of the inhibitor molecules, rate of diffusion of molecules, and ionization of the metallic atoms etc. therefore temperature is a very important adverse condition to corrosion inhibition [16].

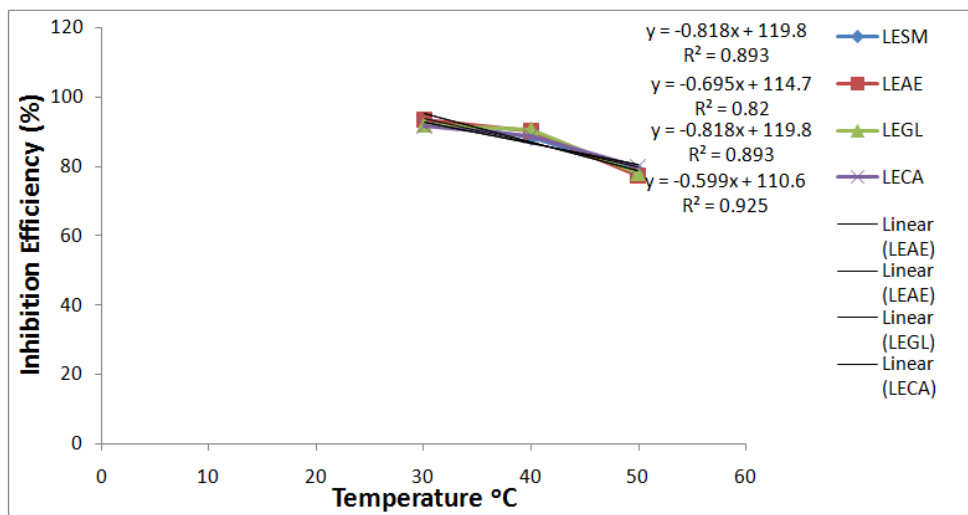


Figure 3 inhibition efficiency of the different inhibitors plotted against temperatures.

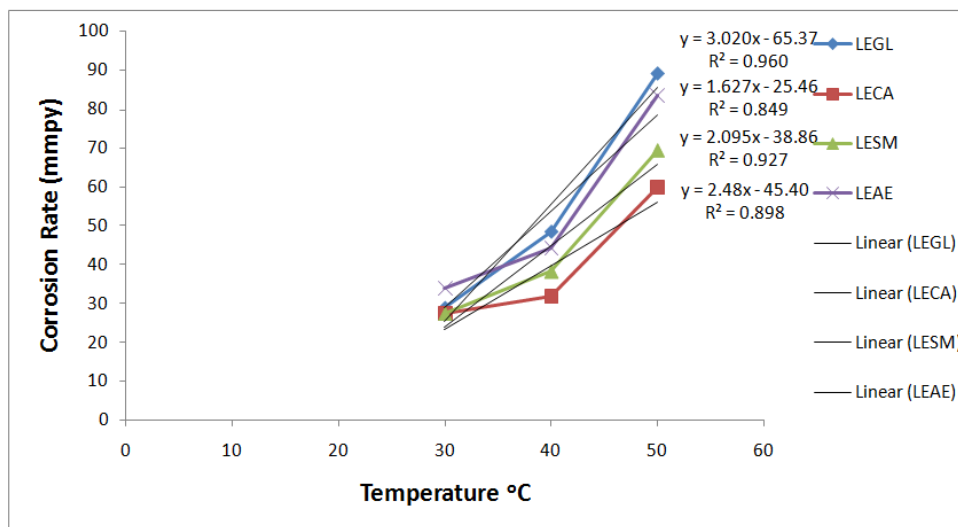


Figure 4 Corrosion rate versus temperature in different inhibitor media

3.3 Adsorption properties of inhibitors

Since the adsorption of inhibitor molecules on the metal surface is the key to metal coverage and protection, parameters such as adsorption constant (K_{ads}), surface coverage and the rate constant of the corrosion reaction were calculated for each inhibitor and their results compared in Tables 1, 2 and 3.

Rate constant (k) at 30°C, 40°C, and 50°C for the reaction was calculated using

$$K = \frac{2.303}{Time} \log \frac{w_i}{w_f} \dots\dots\dots (3)$$

Where w_i and w_f are the initial and final weights of metal coupons.

Adsorption coefficient (K_{ads}) was obtained using,

$$K_{ads} = \frac{\theta}{C(1 - \theta)} \dots\dots\dots (4)$$

Where C is the concentration of the inhibitor

It was observed that both rates K and K_{ads} decrease with increase in concentrations of the four inhibitors showing increase in adsorption with increase in concentration. Table 3 showed that LECA has the highest surface coverage of 0.89 at 50% v/v concentration compared to the other three inhibitors though close values were observed. This indicated a qualitative adsorption and spread on the metal surface by LECA. High surface coverage and sticking probability tend to reduce the site for corrosion reaction on the metal surface [17]. It has been established that among other things, the absorption of corrosion inhibitors on the metal surface depend on the nature and charge of the metal, the chemical structure of the corrosion inhibitor, the type of electrolyte, the distribution of the charge in the molecule and the temperature of reaction medium [14]. In this experiment only *Cola acuminata* showed a percentage inhibition efficiency close to 90% (i.e 89%) at the temperature of 50°C which made it the most effective of the four inhibitors for aluminium.

Table 1. $K_{ads} \times 10^{-2}$ of the inhibitors at different Temperatures

Concentration (%v/v)	LEGL			LESM			LEAE			LECA		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
10	80.90	48.82	20.30	115.00	80.91	28.46	61.43	73.33	30.00	61.43	45.56	14.39
20	66.43	30.71	18.81	066.43	40.45	15.00	57.50	45.00	24.41	50.55	33.46	18.80
30	63.33	26.97	14.21	052.22	33.70	11.16	44.29	33.70	18.89	38.37	30.00	18.89
40	47.50	25.28	12.21	039.17	25.28	10.00	39.17	28.75	14.17	39.17	28.75	16.73
50	42.00	23.00	09.76	038.00	23.00	08.53	38.00	26.57	13.38	48.00	26.57	16.18

Table 2. Rate constant (min^{-1}) $\times 10^{-5}$ Showing Effects of Increase in Temperature

Concentration (%v/v)	LEGL $\times 10^{-5}$			LESM $\times 10^{-5}$			LEAE $\times 10^{-5}$			LECA $\times 10^{-5}$		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
10	14.0	23.4	42.4	9.2	15.0	21.0	12.4	21.3	32.2	17.8	33.6	52.2
20	6.6	27.1	30.4	7.7	13.6	20.4	09.2	17.0	17.4	11.1	25.3	28.0
30	6.4	18.2	24.8	6.8	12.8	17.7	08.4	18.9	22.1	13.7	16.9	21.8
40	6.2	20.0	21.7	7.4	10.0	15.3	06.5	13.3	20.1	07.1	13.7	18.7
50	6.1	12.2	20.8	5.6	04.9	13.4	06.4	10.9	17.9	05.2	12.6	14.5

Table 3. Surface Coverage (θ) of the inhibitors Compared at different temperatures

Concentration (%v/v)	LEGL			LESM			LEAE			LECA		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
10	0.89	0.83	0.67	0.92	0.88	0.74	0.86	0.88	0.75	0.86	0.82	0.59
20	0.93	0.86	0.79	0.93	0.89	0.75	0.92	0.90	0.83	0.91	0.87	0.79
30	0.95	0.89	0.81	0.94	0.91	0.77	0.93	0.91	0.85	0.92	0.90	0.85
40	0.95	0.91	0.83	0.94	0.91	0.80	0.94	0.92	0.85	0.94	0.92	0.87
50	0.95	0.92	0.83	0.95	0.92	0.81	0.95	0.93	0.87	0.96	0.93	0.89

Table 4. Half life of inhibitors $t_{1/2}$ (mins) at different temperatures

Concentration (%v/v)	LEGL $\times 10^3$			LESM $\times 10^3$			LEAE $\times 10^3$			LECA $\times 10^3$		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
10	05.0	03.0	01.6	07.5	04.6	03.3	05.6	03.3	02.2	03.9	02.1	01.3
20	10.5	02.6	02.3	09.0	05.1	03.4	07.5	04.1	03.9	06.3	02.7	02.5
30	10.8	03.8	02.8	10.3	05.4	03.9	08.3	03.7	03.1	05.0	04.1	03.2
40	11.2	03.5	03.2	09.3	07.0	04.5	10.7	05.2	03.4	09.8	05.1	03.7
50	12.0	05.7	03.3	12.3	14.3	05.2	10.9	06.4	03.9	13.4	05.5	04.8

Table 5. Average Rate Constant (K) $\times 10^{-5}$ at different temperature and Activation Energy (Ea) KJmol^{-1}

Temperature	Average $K \times 10^{-5}$				Activation Energy (Ea) kJ mol^{-1}			
	LEGL	LESM	LEAE	LECA	LEGL	LESM	LEAE	LECA
30°C	08.30	07.35	08.56	10.97	30°C-40°C	30°C-40°C	30°C-40°C	30°C-40°C
40°C	20.19	11.24	16.28	20.41	40°C-50°C	40°C-50°C	40°C-50°C	40°C-50°C
50°C	28.02	17.46	22.02	27.01	27.55	37.03	25.39	23.55

The half life of the inhibitors in the corrosion reaction which was first order in nature with respect to inhibitor concentrations was calculated Table 4..

Half life ($t_{1/2}$) at 30°C, 40°C, and 50°C using

$$t_{1/2} = \frac{0.693}{k} \dots\dots\dots (5)$$

The activation energy Ea Table 5 was also determined using the Arrhenius equation below;

The Activation Energy (Ea) (kJ mol⁻¹) of the Reaction

$$E_a = \frac{2.303RT_1T_2(\log k_2/k_1)}{T_2 - T_1} \dots\dots\dots (6)$$

Where T₁ and T₂ are the initial and final temperatures respectively, while K₁ and K₂ are the rate constants at T₁ and T₂ respectively. R is the gas constant = 8.314 Jmol⁻¹ K⁻¹.

Increase in the activation energy with the concentration of the inhibitor shows strong adsorption. Therefore the activation energy of LECA in Table 5 shows that it has the strongest adsorption property compared to others under study. This could be attributed to number and structure of the chemical constituents present. The organic constituents called heteroatoms are electron rich as mentioned earlier in the study background, they are capable of strong electrostatic attraction which holds inhibitors to the metal surface. The length of time the inhibitor spends on the metal surface is a function of the half- life of the particular inhibitor, Table 4.

Table 6.Free Energy of Adsorption ΔG_{ads}(kJmol⁻¹) at different Temperatures

Concentration (%v/v)	LEGL			LESM			LEAE			LECA		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
10	-21.2	-20.6	-18.8	-22.7	-21.9	-19.8	-20.5	-21.6	-19.9	-20.5	-20.4	-18.0
20	-20.7	-19.4	-18.7	-20.7	-20.1	-18.1	-20.3	-20.4	-19.4	-20.0	-19.6	-18.7
30	-20.6	-19.0	-17.9	-20.1	-19.6	-17.3	-19.7	-19.6	-18.7	-19.5	-19.3	-18.7
40	-19.8	-18.9	-17.5	-19.4	-18.9	-16.8	-19.4	-19.2	-17.9	-19.4	-19.2	-18.4
50	-19.1	-18.6	-16.9	-19.3	-18.6	-16.5	-19.3	-17.0	-17.8	-19.9	-19.0	-18.3

Table 7. Corrosion Rate (CR) in millimeter per year(mmpy) x 10⁻³

Concentration (%v/v)	LEGL			LESM			LEAE			LECA		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
10	38.2	52.0	141.5	33.0	31.5	65.7	34.5	45.0	105.9	51.1	71.4	173.9
20	29.6	54.8	088.7	29.9	33.3	80.1	29.2	38.6	057.9	36.4	49.8	086.5
30	24.7	51.0	076.5	28.2	34.6	57.0	28.2	41.9	064.7	37.9	39.5	064.1
40	22.6	47.4	071.0	24.5	29.5	49.0	23.5	34.6	063.9	22.3	30.9	048.6
50	20.1	36.9	068.2	20.9	29.8	47.5	21.5	30.8	053.9	21.3	29.3	043.9

3.4 Corrosion Rate CR (as the evidence of corrosion attack)

The corrosion rate in mm per year for the different inhibitors was calculated using

$$CR(mmpy) = \frac{87.6 \times \Delta W}{DAT} \dots\dots\dots (7)$$

Where D is density of the metal, A is the total surface area cut out during sample preparation and T is the time in hour for the immersion of the corroding metal.

Comparing the corrosion rates (CR), it was observed that LECA has the highest corrosion rate at the initial concentration of 10% v/v and the lowest CR at the concentration of 50% v/v of the four inhibitors as shown in Table 7. The trend of the corrosion rate at concentration of 50% v/v was given as: LECA < LESM < LEAE < LEGL. Since decrease in CR means reduction in the corrosion attack on the metal by the corrosive environment, thus, aluminium is best protected by LECA at the concentration of 50% v/v compared to the other three inhibitors. This could be attributed to the nature of adsorption of LECA which is different from that of the other three inhibitors. The adsorption of LECA tends to chemical absorption as shown in Table 5, the value of the activation energy which is 70.10 kJ mol⁻¹ very close to 80 kJ mol⁻¹ the thresh hold value for chemical adsorption [17]. The negative value of ΔG_{ads} Table 6 exhibited by all the inhibitors is an indication of spontaneous adsorption reactions by the inhibitors on aluminium surface.

$$\Delta G_{ads} = - RT \ln(55.5K_{ads}) \dots\dots\dots (8)$$

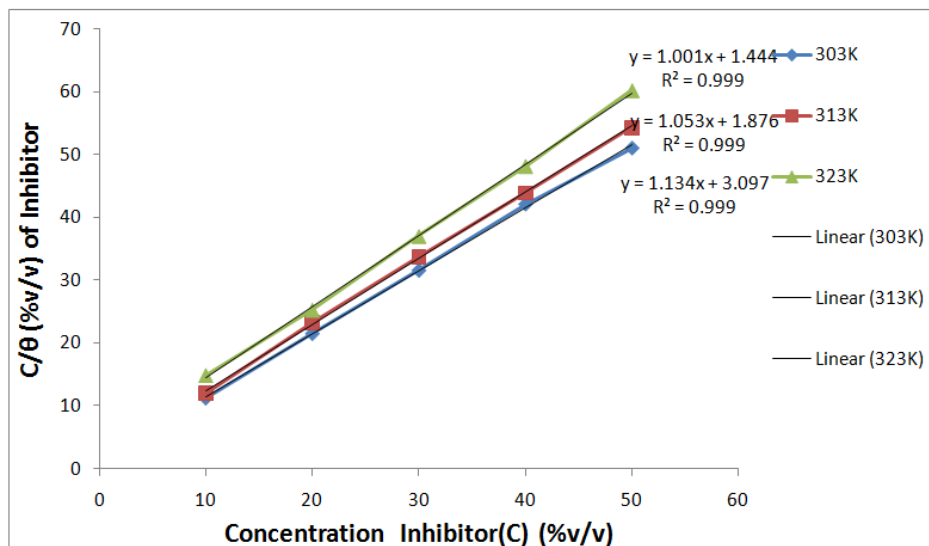


Figure 5 Langmuir adsorption isotherm plot for LEGL on aluminium in 1M HCl solution

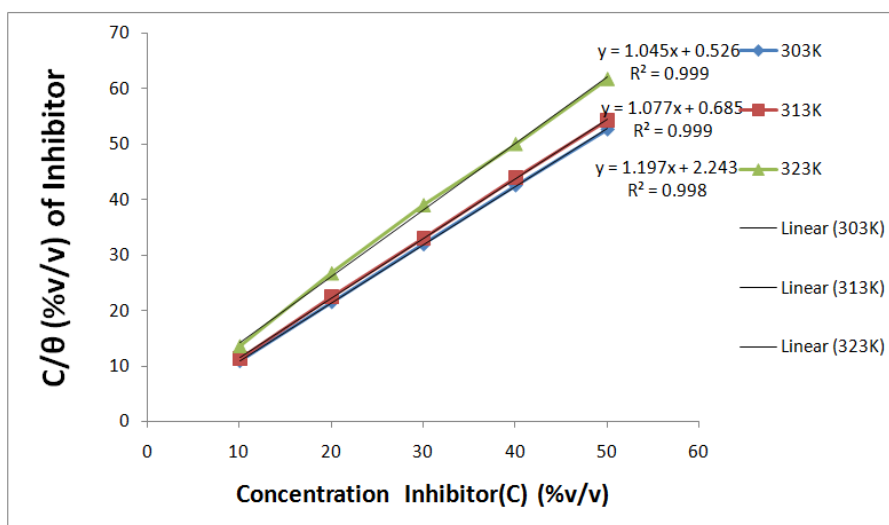


Figure 6 Langmuir adsorption isotherm plot for LESM on aluminium in 1M HCl solution

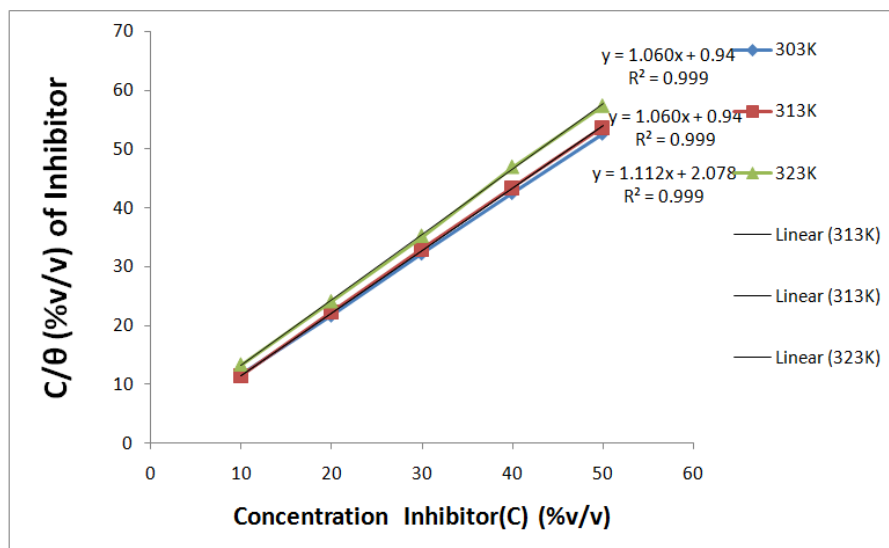


Figure 7 Langmuir adsorption isotherm plot for LEAE on aluminium in 1M HCl solution

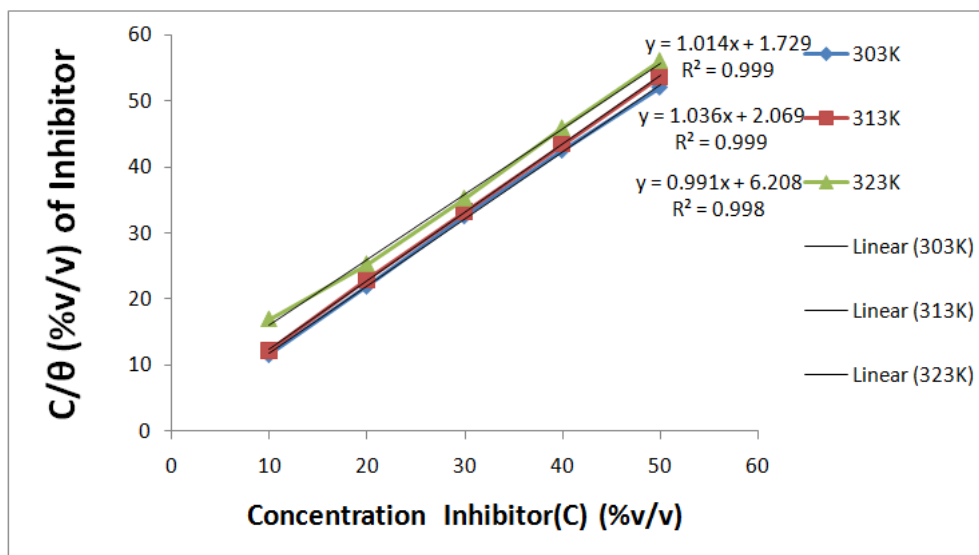


Figure 8 Langmuir adsorption isotherm plot for LECA on aluminium in 1M HCl solutions

Since the adsorption of inhibitor molecules on the metal surface is the key to metal coverage and protection, as mentioned earlier, the nature of adsorption of the different inhibitors was also tested using Langmuir adsorption isotherm. The plots, Figures 5, 6, 7 and 8 showed linearity close to unity for all the inhibitors, suggesting a mono layer adsorption mechanism. This is in confirmation of the high percentage inhibition efficiency exhibited by the inhibitors at the earlier stage of the analysis. This further highlights the fact that most extracts as presented by several authors actually inhibit corrosion to a high extend but care should be taken in monitoring the effects of adverse conditions which could be the reason for the difference in the performance of LECA against the other three inhibitors used in this experiment.

IV. Conclusion

LECA among the studied plant extracts is the best inhibitor for protection of aluminium in HCl corrosive environment at higher temperature.

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