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Inhibition by *Newbouldia leavis* Leaf Extract of the Corrosion of Aluminium in HCl and H_2SO_4 Solutions

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ABSTRACT

The inhibition effect of Newbouldia leavis leaves extract on the corrosion of aluminium in 0.2-1.0 M HCl and 0.1–1.0 M H_2SO_4 solutions was investigated by the gravimetric technique. The results show that Newbouldia leavis is a good inhibitor, and exhibits more efficient in 1.0 M HCl than 0.5 M H_2SO_4. It was shown that the presence of Newbouldia leavis leaf extract inhibited the corrosion of aluminium in the test solutions and the inhibition efficiency depended on the concentration of the plant extract as well as on the time of exposure of the aluminium samples in H_2SO_4 solutions containing the extract. The experimental data complied to the Langmuir adsorption isotherm and the value and sign of the Gibb's free energy of adsorption obtained suggested that inhibitor molecules have been spontaneously adsorbed onto the aluminium surface through a physical adsorption mechanism. The adsorption of Newbouldia leavis on aluminium surface obeys Langmuir adsorption isotherm.

Keywords: Corrosion inhibition, aluminium, adsorption mechanism, *Newbouldia leavis*, free energy of adsorption.

INTRODUCTION

The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [1]. Among numerous inhibitors that have been tested and applied industrially as corrosion inhibitors, those that are non-toxic or low-toxic are now far more strategic than in the recent past. In the 21st century, the research in the field of ‘‘green’’ or ‘‘eco-friendly’’ corrosion inhibitors has been addressed toward the goal of using cheap, effective compounds at low or ‘‘zero’’ environmental impact.

Plant extract is low-cost and environmental safe, and so the main advantage of using plant extract as the corrosion inhibitor is due to both economic and environmental benefits. Up to now, many plant extracts have been used as effective corrosion inhibitors of iron or steel in acidic media, such as *Azadirachta [2]*, *Vernonia amygdalina [3]*, *henna [4–7]*, *Nypa fruticans Wurmb [8]*, *Zenthoxylum alatum [9,10]*, *Damsissa [11]*, *Mentha pulegium [12]*, *olive [13]*, *Phyllanthus amarus [14]*, *Occimum viridis [15,16]*, *lupine [17]*, *Lasianthera africana [18]*, *Strychnos nux-vomica [19]*, *Justicia gendarussa [20]*, *Oxandra asbeckii [21]*, *Ferula assa-foetida [22]*, *coffee [23]*, *fruit peel [24]* and *Halfabar* [25]. Besides steel, aluminium in acidic [26,27] and alkaline media [27–29], zinc in HCl solution [30], and Al–3Mg alloy in neutral NaCl solution [31] were protected against corrosion using some plant extracts. The inhibition performance of plant extract is normally ascribed to the presence in their composition of complex organic species including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products. These organic compounds usually contain polar functions with nitrogen, sulfur, or oxygen atoms as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers. In our laboratory, much work has been conducted to study the inhibition by some plant leaves extract on the corrosion of steel in acidic media. It has been reported that the leaves extracts of *Jasminum nudiflorum Lindl*. [32], *Acer buergerianum* [33] and *Phyllostachys sulphurea* [34] behave as good inhibitors for steel in 1.0 M HCl solution. Moreover, extensive work has been done in both acidic and alkaline media using *Euphorbia hirta* and *Dialum guinnense* leave extracts as inhibitors [35,36]. The inhibitive performance could be attributed to adsorption of flavonoids on aluminium surface. In order to extend the earlier work, *Newbouldia leavis* leaf extract is chosen to use as the corrosion inhibitor on the basis of *Newbouldia leavis* is rich in flavonoids [37].

The inhibiting effect of *Newbouldia leavis* plant extract on aluminium alloy (AA8011) in 1.0 M HCl and 0.5 M H_2SO_4 was investigated. This study has dual purposes, first to establish the effectiveness of the plant extracts as corrosion inhibitors and secondly to attempt deduction of the inhibition mechanisms through adsorption isotherms. Moreover, this work seeks a comparison of the two environments used. This work is done at high concentration limit to determine optimum concentration of the extract. The equation for corrosion rate is given by

$$C = {}^{k\Delta W}\!/_{\rho A t} \qquad (1)$$

Where k = Rate constant equal 534 *mpy*; *mpy* means mils per year
W = Weight loss in mg
ρ = Density of material in g/cm^3
T = Exposure time in hours
A = Exposed area of coupon in^2
noting that 1 in^2 = 6.5416 cm^2.

MATERIALS AND METHODS

Aluminium alloy AA8011 specimens having weight percentage composition as follows; Si-0.240%, Fe-0.241%, Cu-0.035%, Mn-0.102%, Ti- 0.019%, Pb-0.014%, Zn-0.043% and the remainder being Al were used. The specimens were of dimensions 2 cm x 2 cm and thickness 1.32 mm. The alloy specimen were polished mechanically using SiC emery papers of grade nos 220, 400 and 600, washed thoroughly with distilled water and degreased with ethanol and acetone. The specimens were then air dried before being immersed in the acid solution. The blank corrodent was 0.5 M H_2SO_4 and 1.0 M HCl solutions. Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried and ground plant material for 3 hours in the 0.5 M H_2SO_4 and 1.0 M HCl. The solutions were cooled and then filtered and stored. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range of 0.1 - 0.4 g/L using excess acid as solvent at room temperature and 60°C using water bath.

Gravimetric experiment

The cleaned and dried specimens were weighed before immersion into the respective test solutions of 0.5 M H_2SO_4 and 1.0 M HCl using JA 1003A electronic weighing balance with the accuracy of ±0.005. Tests were conducted with different concentrations of inhibitor. At the end of the tests, the specimens were carefully washed in absolute ethanol having used nitric acid to quench further corrosion from taking place, and then reweighed. Triplicate experiments were performed in each case and the mean values reported.

RESULTS AND DISCUSSION

Gravimetric technique and corrosion rates

The corrosion rates of the aluminium in 0.5 M H_2SO_4 and 1.0 M HCl in the absence and presence of *Newbouldia leavis* leaf extract were determined at room temperature (303K). Figures 1 and 2 shows the time variation of corrosion rates of the aluminium in 0.5M H_2SO_4 and 1M HCl with and without the *Newbouldia leavis* leaf extract, while Figures 3 and 4 shows the variation of the corrosion rates of the aluminium in 0.5M H_2SO_4 and 1M HCl with inhibitor concentration. Figures 3 and 4 show clearly that the leaf extract retards the corrosion rate of the aluminium in the test solutions.

Figure 5 illustrates the variation of the corrosion rates of the aluminium in 0.5 M H_2SO_4 and 1M HCl with inhibitor concentration for an exposure time of 8 hours. Moreover, it can be seen from Figure 5 that the corrosion rate decreases with increase in the concentration of the inhibitor. The inhibition efficiency of the *Newbouldia leavis* leaf extract on the corrosion of the aluminium in 0.5 M H_2SO_4 and 1M HCl containing different concentrations of the leaf extract was computed by using the relation [38,39,40].

$$I\% = \left(1 - {}^{\rho_{inh}}/_{\rho_{blank}}\right) \qquad (2)$$

where I% represents the inhibition efficiency expressed in percentage, ρ_{inh} is the corrosion rate in the presence of the inhibitor while ρ_{blank} is the corrosion rate in the absence of inhibitor. Optimum values of 92% at 0.4g/L and 95% at 0.4g/L for 0.5 M H_2SO_4 and 1M HCl respectively for concentration of *Newbouldia leavis* extract was obtained as shown in Figure 5. The results show that *Newbouldia leavis* leaf extract is a good inhibitor, and exhibits more efficient in 1.0 M HCl than 0.5 M $H_2 SO_4$.

Inhibition efficiency

Clearly, the inhibition efficiency of *Newbouldia leavis* leaf extract increases with exposure time for the inhibitor concentration considered. This result is consistent with the findings of [36] who showed that the inhibition efficiency of *Euphorbia hirta* in the corrosion of the aluminium alloys AA3003 in 0.5 M HCl increases with exposure time. As shown in Figure 5, the inhibition efficiency increases with increase in inhibitor concentration, tending to saturate at higher values of inhibitor concentration. This indicates that the effectiveness of the *Newbouldia leavis* leaf extract in retarding the corrosion rate of aluminium in the test solutions does not improve indefinitely with increase in inhibitor concentration. A point is reached at which an increase in the inhibitor concentration produces only a very small increase in inhibition efficiency. A similar conclusion has been reached by [41, 42] who studied the inhibitive effect of thiosemicarbozides on the corrosion of steel in phosphoric acid and the inhibitive effect of Solanum melongena L. Leaf extract on the corrosion of aluminium in tetraoxosulphate (VI) acid respectively.

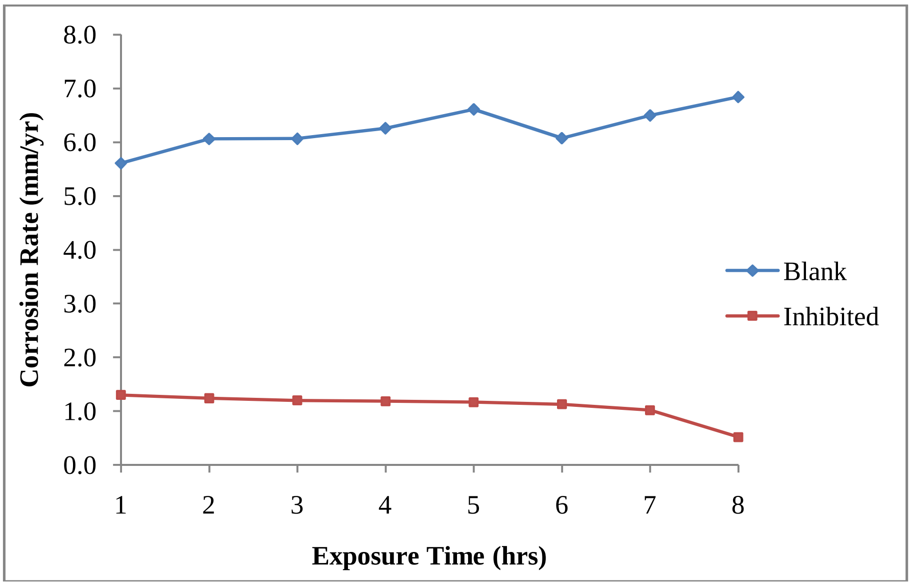

Figure 1. Time variation of the corrosion rates of aluminium in 0.5M H_2SO_4. The blank and inhibited with *Newbouldia leavis* leaf extract of concentration 0.4g/L.

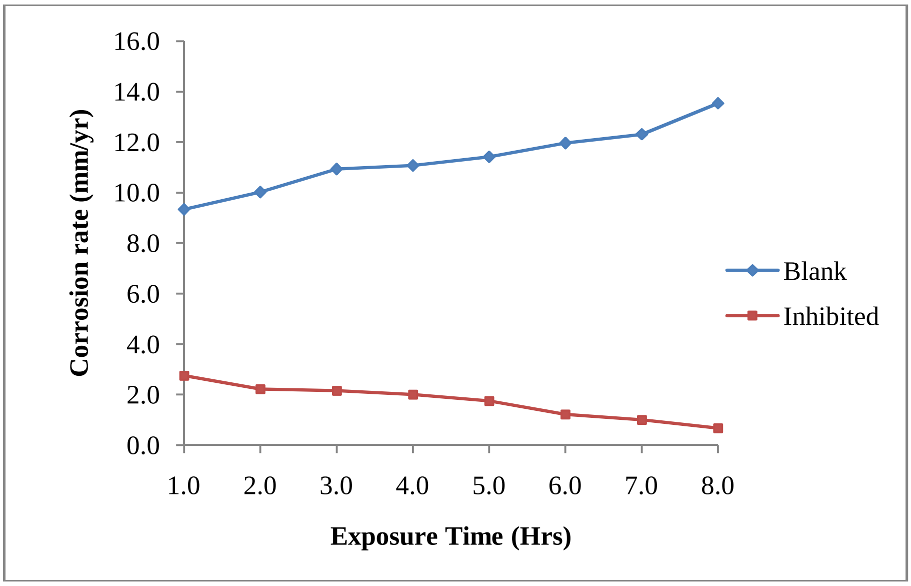

Figure 2. Time variation of the corrosion rates of aluminium in 1.0 M HCl. The blank and inhibited with *Newbouldia leavis* leaf extract of concentration 0.4g/L.

The result that the inhibition efficiency of *Newbouldia leavis* leaf extract increases with increase in inhibitor concentration suggests that some of the molecules of the inhibitor are adsorbed on the metal surface thereby protecting the "covered" surface from further corrodent attack. Increasing the inhibitor concentration increases the degree of surface coverage, θ, of the metal surface defined as:

$$\theta = 1 - \frac{\rho_{inh}}{\rho_{blank}} \qquad (3)$$

The *Newbouldia leavis* leaf extract consists of a mixture of complex organic components including flavonoids, several phenolic compounds (β-carotene – linoleic acids) and some other organic compounds. The plant extract also contains some nutritional minerals including potassium, magnesium, copper and zinc [43-46].

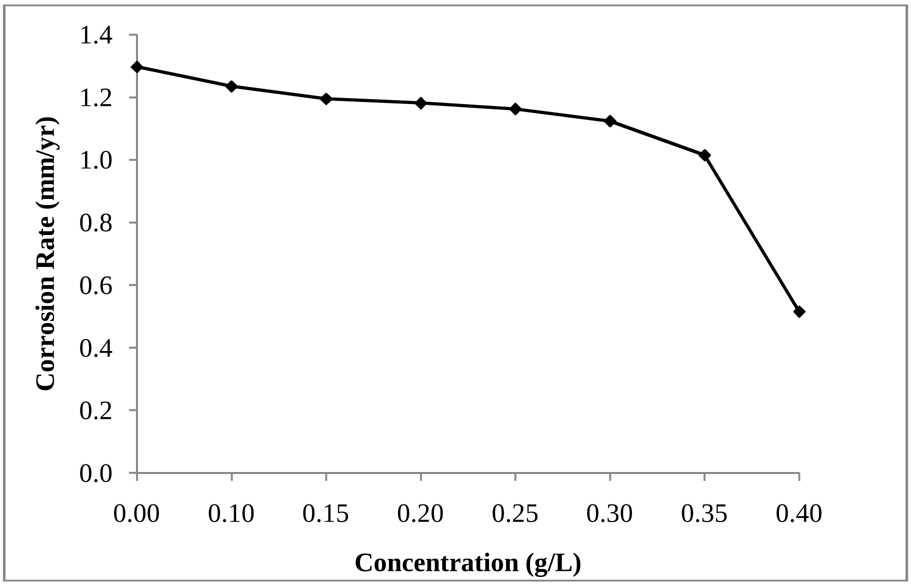

Figure 3. Variation of corrosion rate of aluminium in 0.5M H_2SO_4 with different concentrations of *Newbouldia leavis* extract.

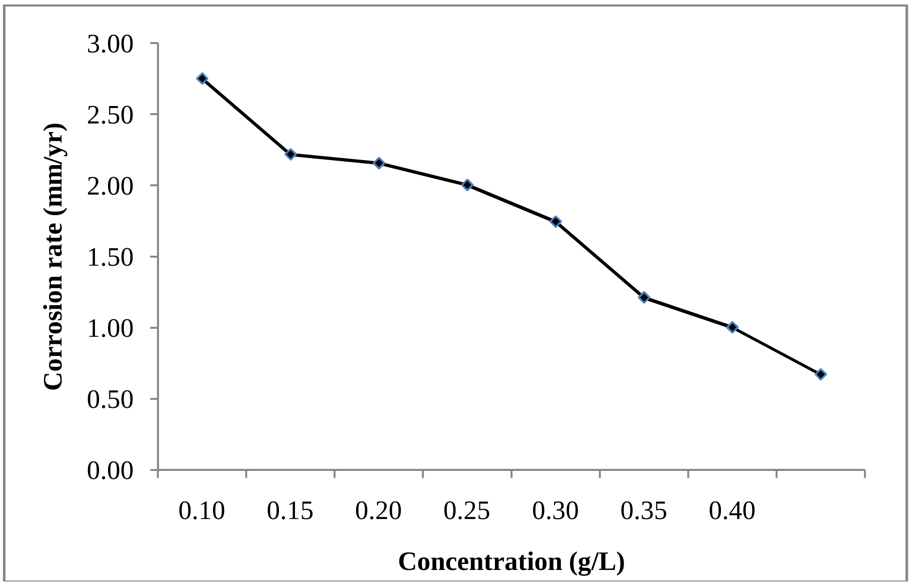

Figure 4. Variation of corrosion rate of aluminium in 1.0 M HCl with different concentrations of *Newbouldia leavis* extract.

It is interesting to note that a number of the above named organic compounds exhibit antioxidant activity. For example, nasunin (a flavonoid), β-carotene – linoleic acids (phenolic compounds) are antioxidants. Results of earlier studies suggest that tannins and some antioxidant compounds in plant extracts contribute to inhibition of steel corrosion in some acidic medium [15, 46, 47]. In fact, plant/leaf extracts which have proven corrosion inhibiting abilities in corrosive media are known to contain one or more more of the following organic substances, namely tannins, triterpenoids, flavonoids, amino acids, alkaloids, saponins, phenols, glycosides, essential oils, carotenoids, β-carotene, ascorbic acid, crude proteins among others [15, 35, 38, 39, 40]. Some research workers [48-50] have demonstrated that amino acids are indeed effective corrosion inhibitors. It is therefore reasonable to expect that the presence of amino acids, antioxidant organic compounds (nasunin – a flavonoid, caffeic and chlorogenic acids –phenolic compounds), crude proteins or indeed any other of the complex organic substances in the *Newbouldia leavis* leaf extract could in combination with the other constituents be responsible for the inhibition of aluminium corrosion in 0.5 M H_2SO_4 and 1 M HCl. Moreover, the presence of some metallic ions particularly Mg^{2+} may enhance the corrosion inhibiting action of the extract. This is because it has been observed that some inorganic ions particularly Ca^{2+}, Mg^{2+} and Zn^{2+} ions synergistically increase the inhibition efficiency of organic substances [38, 51, 52]. Nevertheless, it is not possible at this point to identify the particular constituent or group of constituents of the plant extract that are adsorbed onto the metal surface. In any case, the adsorbate molecules on the metal surface constitute a barrier to charge and mass transfer between the metal and the corrodent, thereby protecting the metal surface from corrodent attack. The larger the degree of surface coverage resulting from enhanced adsorption of molecules of the plant extract, the greater the protection to corrosion offered by the inhibitor [39].

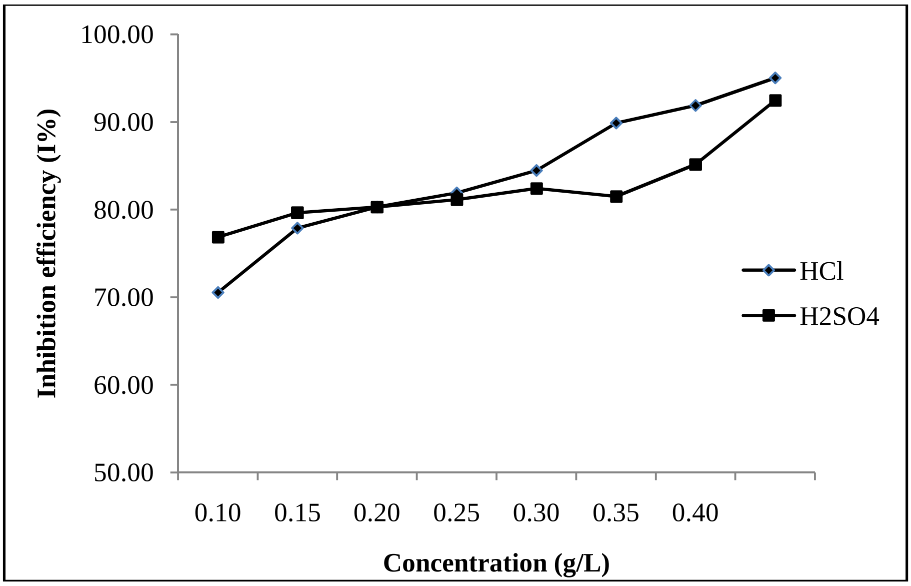

Figure 5. Variation of inhibition efficiency with concentration of *Newbouldia leavis* leaf extract for aluminium in 0.5 M H_2SO_4 and 1.0 M HCl

Table 1: Values of Langmuir isotherm parameters for aluminium alloy

Plant extract	Intercept	Slope	K (x 10^{-4})	R^2	ΔG^o ($kJmol^{-1}$)
NL in 0.5M H_2SO_4	1.09	0.02	8.3	0.989	-7.76
NL in 1M HCl	0.032	0.05	9.7	0.994	-11.85

Table 2: Calculated values of inhibition efficiency (I%), apparent activation energy (E_a) and heat of adsorption (Q_{ads}) of *Newbouldia leavis* extract on AA8011 aluminium alloy in 0.5M H_2SO_4 at different temperatures

Extract concentration (g/L)	Inhibition efficiency (I%)		E_a ($kJmol^{-1}$)	Q_{ads} ($kJmol^{-1}$)
	30°C	60°C		
Blank				
0.10	76.86	50.20	62.85	-559.89
0.15	79.62	58.65	54.04	-506.36
0.20	80.29	61.69	41.52	-463.76
0.25	81.41	65.35	51.76	-421.06
0.30	82.41	69.72	38.16	-355.01
0.35	85.16	71.14	29.26	-422.33
0.40	92.47	76.25	31.41	-670.54

Table 3: Calculated values of inhibition efficiency (I%), apparent activation energy (E_a) and heat of adsorption (Q_{ads}) of *Newbouldia leavis* extract on AA8011 aluminium alloy in 1M HCl at different temperatures

Extract concentration (g/L)	Inhibition efficiency (I%)		E_a (kJmol^{-1})	Q_{ads} (kJmol^{-1})
	30°C	60°C		
Blank				
0.10	77.54	52.32	17.78	-452.78
0.15	80.29	56.04	14.86	-582.38
0.20	81.91	59.86	9.65	-580.64
0.25	84.47	63.24	37.14	-557.65
0.30	89.86	61.45	41.63	-575.30
0.35	91.86	69.80	25.52	-857.31
0.40	95.03	73.45	22.46	-748.22

Table 4: Major constituents of *Newbouldia leavis*

Plant	Major constituents
Newbouldia leavis	flavonoids, tannins, terpenes, steroidal and cardiac glycosides

[45, 46].

Adsorption considerations and Adsorption Isotherms

In the situation where it is suspected that the inhibition of metal corrosion occurred as a result of the adsorption of molecules of plant extracts onto the metal surface, it is instructive to investigate the possible adsorption mode by testing the experimental data obtained with several adsorption isotherms. Such an exercise will greatly elucidate one's understanding of the corrosion inhibition mechanism. The generalized expression for several adsorption isotherms usually tested is of the form [41, 55, 56].

$$f(\theta, x)\exp(-\alpha\theta) = kC \qquad (4)$$

where f (θ, x) is the configuration factor whose functional form depends on the physical model adopted and assumptions made in deriving the isotherm, θ is the degree of surface coverage, x is known as the size ratio which gives the number of water molecule replaced by the inhibitor molecule, α is a molecular interaction parameter whose value depends on the type of molecular interactions in the adsorption layer and the degree of homogeneity of the surface, C is the inhibitor concentration while k is the adsorption equilibrium constant which is temperature dependent according to the relation [41, 56-59].

$$k = \frac{1}{55.5}\exp\left(-\frac{\Delta G_{ads}}{RT}\right) \qquad (5)$$

where ΔG_{ads} is the standard free energy of adsorption, R, is the molar gas constant and T is absolute temperature. Several adsorption isotherms were tested for fit with the experimental data. These include the Langmuir, Frumkin, Temkin, Freundlich and the Flory-Huggins isotherms. Incidentally, the Langmuir isotherm gave the best fit with the experimental data. The Langmuir isotherm equation is of the form [39, 47, 55-57]:

$$C/_{\theta} = 1/_{k} + C \qquad (6)$$

From a plot of $\frac{C}{\theta}$ against C, a straight line graph was obtained with a slope of 0.02 and an intercept of 1.09 on $\frac{C}{\theta}$ axis for 0.5 M H_2SO_4. The 1M HCl environment, a slope of 0.05 and an intercept of 0.032 were obtained. The coefficient of correlation, R^2, gave the degree of fit between the experimental data and the isotherm equation. The values obtained was found to be

0.989 and 0.994 for 0.5M H_2SO_4 and 1 M HCl respectively, which indicates a very good fit between the Langmuir isotherm and the experimental data. Figures 6 and 7 shows the Langmuir isotherm plot for the inhibition of the corrosion of aluminium in 0.5 M H_2SO_4 and 1M HCl by *Newbouldia leavis* leaf extract respectively. Using the value of intercept obtained from the graph and equations 4 and 5 a value of -7.76 $kJmol^{-1}$ and -11.85 $kJmol^{-1}$ was obtained for G^{o}_{ads} for 0.5M H_2SO_4 and 1 M HCl respectively. The very good fit of the experimental data with the Langmuir adsorption isotherm suggests that the Langmuir adsorption model is applicable in the corrosion inhibition mechanism. In the derivation of the Langmuir isotherm, it was assumed that the adsorption sites on the metal surface are uniformly distributed and energetically identical and that the maximum number of adsorbed molecules per site is one, implying a case of monolayer adsorption. Additionally, it was assumed that adsorbate molecules do not interact with one another. The negative values of G^{o}_{ads}, the Gibb's free energy of adsorption, obtained means that the adsorption process was spontaneous.

The values of G^{o}_{ads} obtained in this study is low enough for one to attribute the adsorption process as due to an electrostatic interaction between the atoms/ions on the metal surface and the adsorbate molecules [60], a mechanism which is consistent with physical adsorption (physiosorption). The obtained value of the slope of the Langmuir isotherm plot of 1.09 which is about unity (the expected value for ideal Langmuir isotherm model) authenticates the physisorption. The value of the standard free energy of adsorption is still within the energy range characterising the physisorption model of adsorption. It has been pointed out [56, 61-63] that generally, values of G^{o}_{ads} up to -20 $kJmol^{-1}$ are consistent with physical adsorption. The interactions involved in this mechanism are more or less weak electrostatic interactions between metal atoms and adsorbate species. In fact, the adsorption energies involved have the same range of energy values as the van der Waals bond energies [60]. However, values of G^{o}_{ads} which are more negative than - 40 $kJmol^{-1}$ are associated with chemical adsorption, also called chemisorption. The mechanism involves charge sharing or charge transfer between the atoms of the metal and the adsorbate molecules. The associated bonds are strong and the corresponding bond energies could be as large as those characteristics of primary bonds in solids [60].

Effect of Temperature

The apparent activation energies (E_a) for the corrosion process in absence and presence of inhibitor were evaluated from Arrhenius equation.

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303\mathrm{R}}\left(\frac{1}{\mathrm{T}_1} - \frac{1}{\mathrm{T}_2}\right) \qquad (7)$$

On the other hand, estimates of the heats of adsorption (Q_{ads}) were obtained from the trend of surface coverage with temperature as follows [64,65]

$$Q_{ads} = 2.303\mathrm{R}\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{\mathrm{T}_1\mathrm{T}_2}{\mathrm{T}_2 - \mathrm{T}_1} \qquad (8)$$

ρ_1 and ρ_2 are the corrosion rates in temperatures T_1 and T_2, respectively while θ_1 and θ_2 are the degrees of surface coverage at temperature T_1 and T_2 and R is the gas constant.

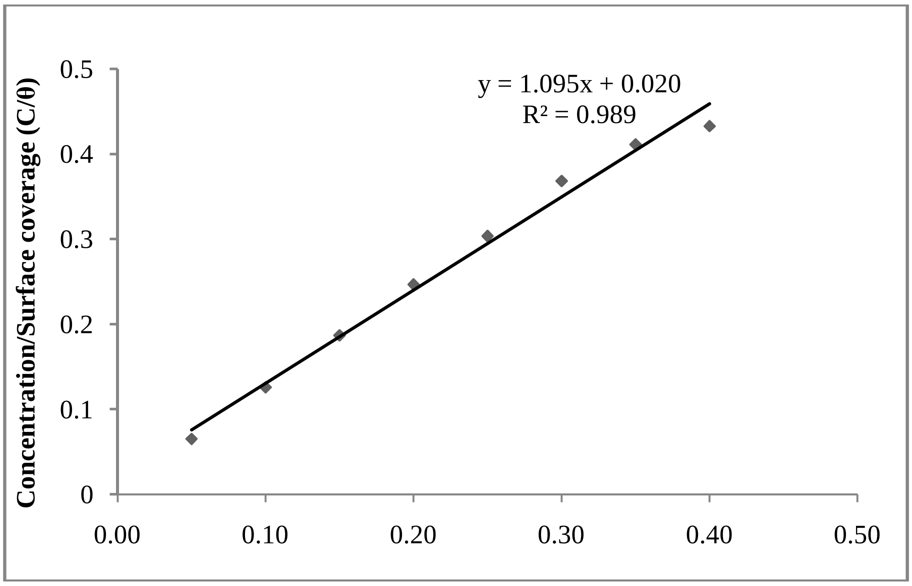

Figure 6. Langmuir adsorption isotherm for inhibition of aluminium in 0.5M H_2SO_4 by *Newbouldia leavis* leaf extract.

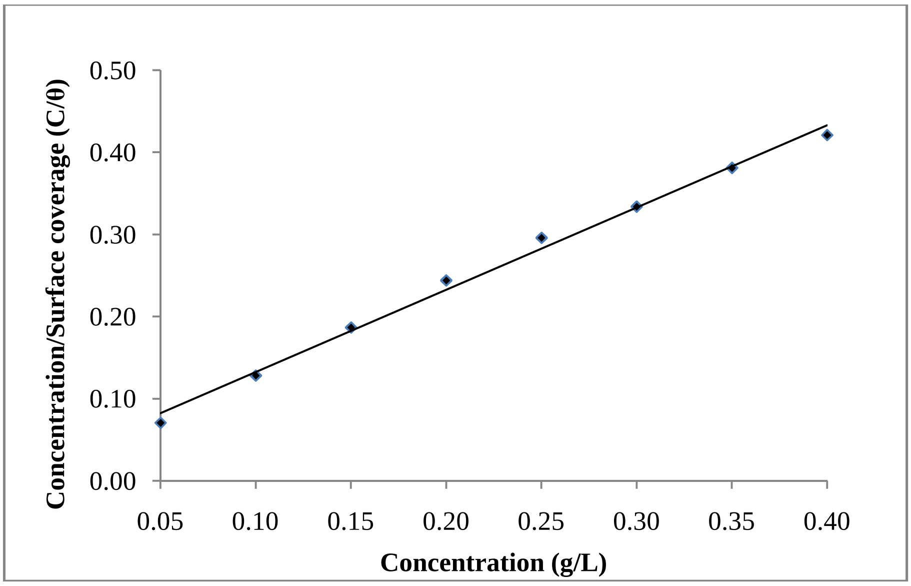

Figure 7. Langmuir adsorption isotherm for inhibition of aluminium in 1.0 M HCl by *Newbouldia leavis* leaf extract.

CONCLUSION

It has been shown in this study that the addition of *Newbouldia leavis* leaf extract to H_2SO_4 and HCl reduces the corrosion rate of aluminium in the acid. The inhibition efficiency of the plant extracts increases with increase in concentration although it decreases with rise in temperature. The HCl environment exhibits more efficient than H_2SO_4. The experimental data obtained are best described by the Langmuir adsorption isotherm, signifying the formation of a single layer of inhibitor molecules onto aluminium alloy surface. Moreover, values of the Gibb's free energy of adsorption obtained suggests that the spontaneous physical adsorption of the plant extract molecules is the most likely inhibitory mechanism responsible for the reduction of the corrosion rate of the aluminium in 0.5M H_2SO_4 and 1 M HCl containing *Newbouldia leavis* leaf extract.

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