

The Effects of Some Plant Extracts on Corrosion and Adsorption Mechanism Process of Aluminium in alkaline Solution

¹L.A. Nnanna*, ²B.N. Onwuagba, ²I.M. Mejehe, ²K.B. Okeoma

¹Department of Physics/ Electronics, Abia State Polytechnic, P.M.B. 7166, Aba, Nigeria

²Department of Physics, Federal University of Technology, P.M.B. 1526, Owerri, Nigeria

lebennanna@yahoo.com

Abstract

Inhibition of corrosion of aluminium in aqueous solutions of sodium hydroxide in the presence of *Euphorbia hirta* and *Dialium guineense* plant extracts was studied in relation to the concentration of inhibitor, concentration of corrosive medium at various temperatures applying weight loss technique. The plant extracts tested were found to be good inhibitors for aluminium alloy (AA3003) corrosion in aqueous solutions of sodium hydroxide in the studied concentration range of 0.25M. Due to the adsorption of the extract molecules on the metal surface, the inhibition efficiency increases with increasing extract concentration. *Dialium guineense* extract shows the best inhibition capability for aluminium corrosion in sodium hydroxide, probably, this is due to the planer orientation of the adsorbed extract molecules. Inhibition efficiency of the inhibitors tested increases with decreasing sodium hydroxide concentrations. The higher the temperature, the lower was the inhibition efficiency, which is due to the fact, that the rate of corrosion of aluminium is higher than the rate of adsorption.

Keywords: corrosion, sodium hydroxide, inhibitors, aluminium, weight loss.

Introduction

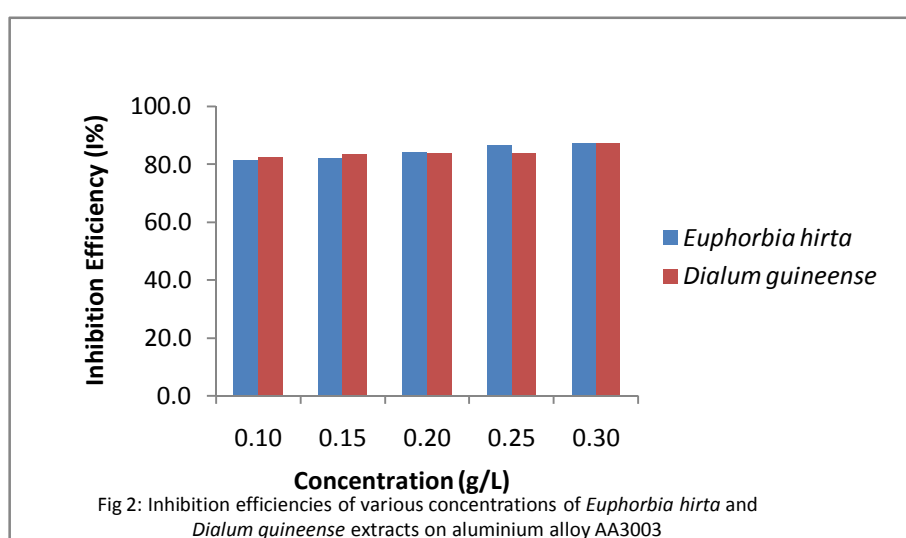
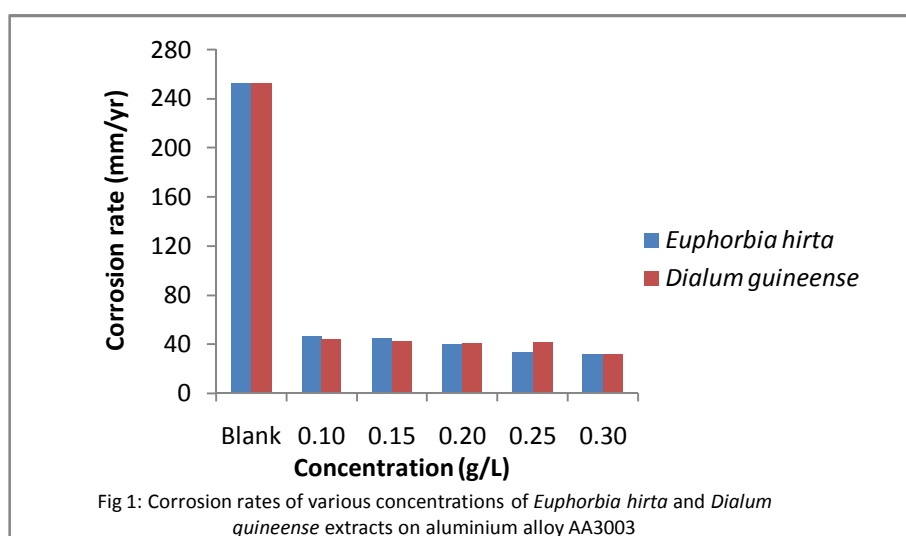
Due to the lightweight and mechanical strength, aluminium and its alloys are very attractive materials for engineering applications. The interest of these materials arises from their importance in the recent civilization. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents the corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosive media 'Saleh et al [1]'. Heteroatoms in the structure of inhibitor molecules, such as oxygen(O), nitrogen(N), phosphorous(P), sulphur(S) and the presence of aromatic rings or triple bonds enhance the adsorption process. It has been reported that the inhibition efficiency increases in the order: $O < N < S < P$ 'Maayta [2], Thomas [3], Donnelly et al [4], Tadros [5], Subramanyam [6]'. Corrosion inhibition of aluminium and its alloys was the subject of numerous studies 'Fouda et al [7], Elbasiouny et al [8], Sanakarapavinasam et al [9], Scholl et al [10], Khamis et al [11]'. The exploration of natural products of plant origin as inexpensive, eco-friendly corrosion inhibitors is an essential field of study. In addition to being environmentally friendly and ecologically acceptable, plant products are low cost, readily available and renewable sources of materials. The extracts from their leaves, barks, seeds, fruits and roots comprise of mixtures of organic compounds and some have been reported to function as effective inhibitors of metal corrosion inhibition efficiencies using the plant extracts of *Occimum viridis* 'Oguzie [12]', *Telferia occidentalis* 'Oguzie [13]', *Azadirachta indica* 'Oguzie [14]', and *Hibiscus sabdariffa* 'Oguzie [15]'. The corrosion inhibition efficacy of these extracts is normally ascribed to the presence, in their composition, of complex organic species such as tannins, alkaloids, essential oils, flavonoids and nitrogen bases. The inhibiting effect of *Euphorbia hirta* and *Dialium guineense* plant extracts on aluminium alloy (AA3003) in 0.25M NaOH 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. Mass loss can be determined gravimetrically, volumetrically and radiometrically, all are the direct measures of corrosion of these, gravimetric or mass loss are most used for inhibitor testing.

Experimental Procedure

Aluminium alloy specimens having weight percentage composition as follows; Si-0.362%, Fe-0.54%, Cu-0.077%, Mn-1.219%, Ti-0.026%, Pb-0.063%, Zn-0.004% and the remainder being Al were used.

The inhibition efficiency of aluminium in aqueous solutions of sodium hydroxide (NaOH) by using *Euphorbia hirta* and *Dialium guineense* plant extracts as inhibitors was determined by the gravimetric technique. The specimens were of dimension 2 cm × 2 cm and thickness 1.32 mm. The aluminium alloy specimens 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, air dried before being immersed in the alkaline solution. The blank corrodent was 0.25M NaOH solution. Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried and ground plant material for 3 hours in the 0.25M NaOH. The solutions were cooled and then filtered and stored. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range of 0.1g/L to 0.3g/L using excess alkaline as solvent. The cleaned and dried specimens were weighed before in the respective test solution using electronic balance of series JA 1003A with the accuracy of ± 0.005 . Total immersion period was 4 hours. 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



The Langmuir Isotherm for AA3003 Aluminium Alloy

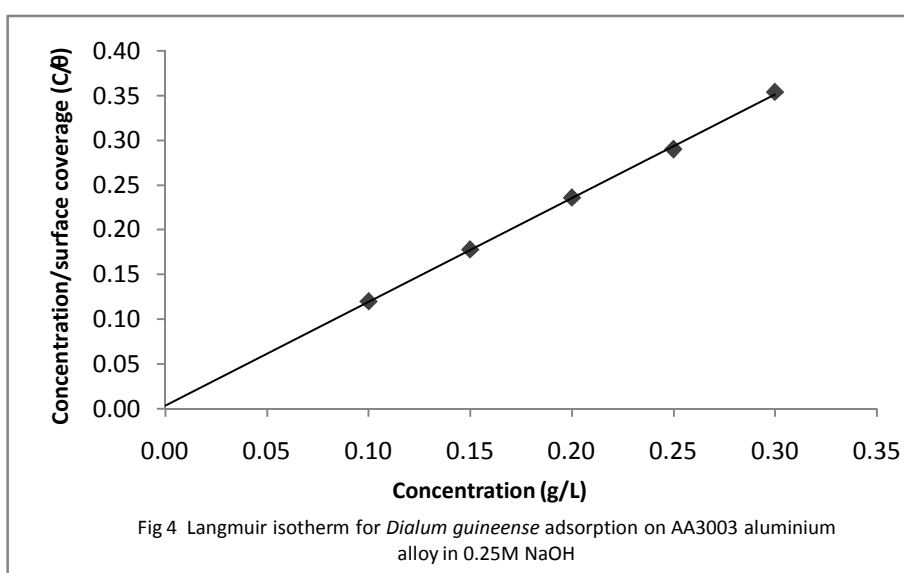
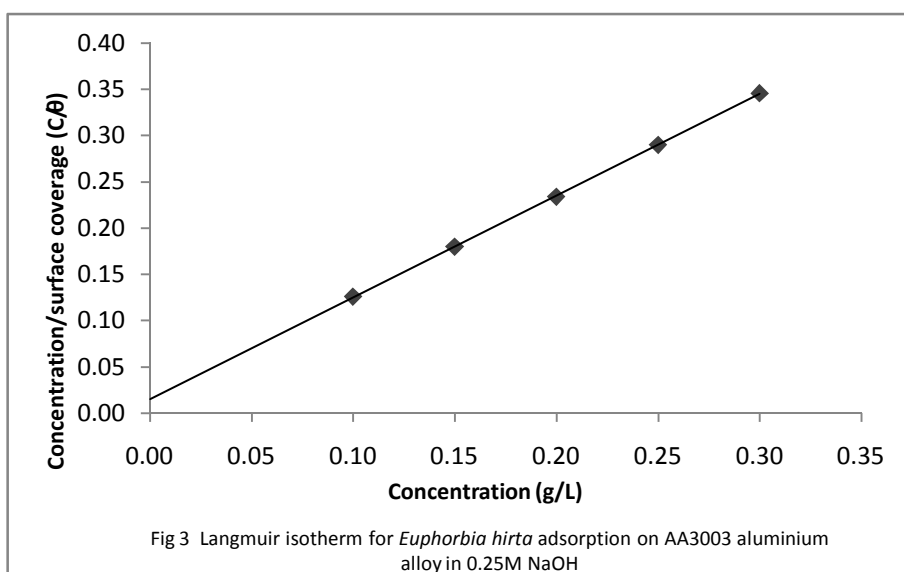


Table 1: Values of Langmuir parameters for AA3003 aluminium alloy

Plant Extract	Intercept	Slope	K	R ²	ΔG°(kJmol ⁻¹)
EH in NaOH	0.0152	1.10	65.79	0.9999	-20.45
DG in NaOH	0.0036	1.11	277.78	0.9994	-24.04

The Temkin Isotherm for AA3003 Aluminium Alloy

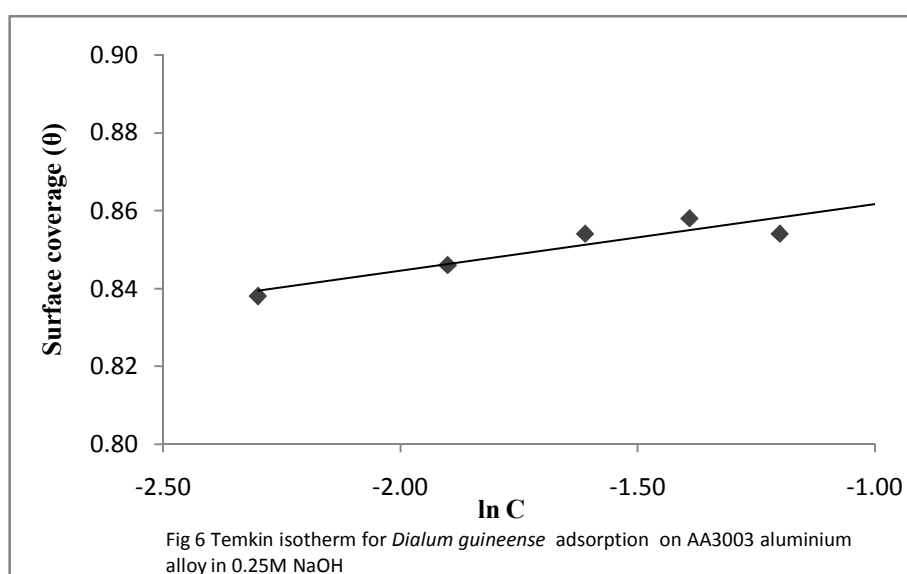
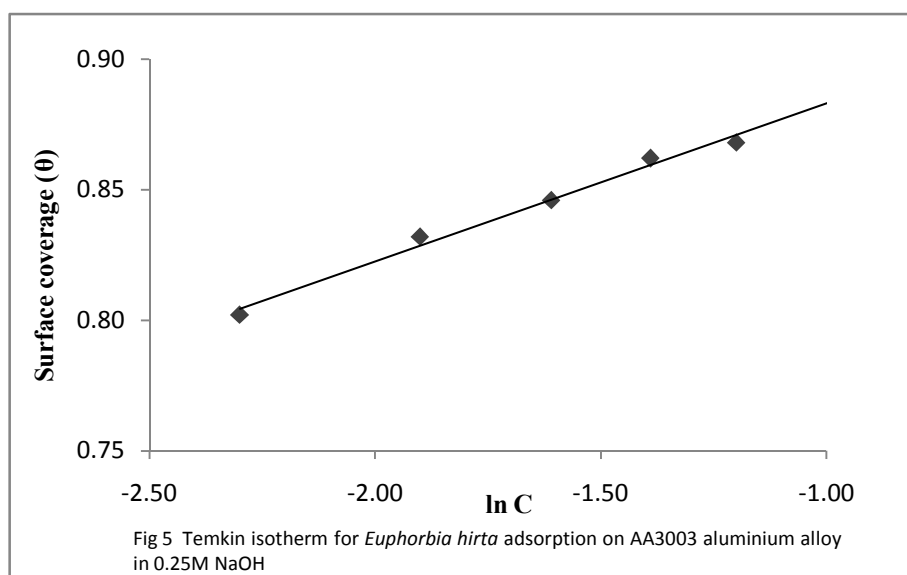


Table 2: Values of Temkin parameters for AA3003 aluminium alloy

Plant Extract	Intercept	Slope	K	R ²	ΔG° (kJmol ⁻¹)
EH in NaOH	0.94	0.06	5.84×10^6	0.9883	-48.86
DG in NaOH	0.88	0.02	–	0.8561	-138.34

Table 3: Calculated values of inhibition efficiency (I%), apparent activation energy (E_a) and heat of adsorption (Q_{ads}) of Euphorbia hirta extract on AA3003 aluminium alloy in 0.25M NaOH at different temperatures

Extract Concentration	Inhibition Efficiency (I%)		$E_a(kJmol^{-1})$	$Q_{ads}(kJmol^{-1})$
	30°C	60°C		
Blank			4.61	
0.1	81.6	69.4	48.55	-5.57
0.15	82.2	73.2	54.54	-4.36
0.2	84.3	76.8	37.96	-4.02
0.25	86.7	80.4	84.17	-3.85
0.3	87.5	83.1	44.05	-2.94

Table 4: Calculated values of inhibition efficiency (I%), apparent activation energy (E_a) and heat of adsorption (Q_{ads}) of Dialium guineense extract on AA3003 aluminium alloy in 0.25M NaOH at different temperatures

Extract Concentration	Inhibition Efficiency (I%)		$E_a(kJmol^{-1})$	$Q_{ads}(kJmol^{-1})$
	30°C	60°C		
Blank			4.61	
0.1	82.7	75.2	17.97	-3.78
0.15	83.5	77.6	22.27	-3.15
0.2	83.7	77.9	6.41	-3.13
0.25	83.7	80	3.76	-2.08
0.3	87.5	82.4	45.39	-3.34

Discussion

Weight losses and corrosion rates

The weight loss of the aluminium alloy in 0.25M NaOH with and without the various concentrations of plant extracts was determined after 4 hours of immersion at 30° C. The corrosion rate was evaluated using Equation 1

$$\rho = \frac{k\Delta W}{ADt} \quad 1$$

Where ΔW is weight loss, ρ is the density of the metal, A is the cross sectional area of the metal and t is the time of exposure in year. The corrosion rate is measured in mm/yr. Equation 2 determines the inhibition efficiency (I%) where ρ_{blank} and ρ_{inh} are the corrosion rates of aluminium alloy (AA3003) without and with the inhibitor, respectively. Values of the inhibition efficiency obtained are shown in figure 2.

$$I\% = \left(1 - \frac{\rho_{inh}}{\rho_{blank}}\right) \times 100 \quad 2$$

Corrosion rate values of the alloy decrease when the inhibitor concentration increases. The inhibition efficiency increases with increasing inhibitor concentration, reaching optimum value of about 87.5% at 0.3g/L concentration of Euphorbia hirta and Dialium guineense extracts as shown in Figure 2.

Inhibition efficiency and adsorption considerations

The characterization of the corrosion rate of aluminium alloy in the different inhibitor/ corrodent solutions was carried out by an assessment of inhibition efficiency using equation 2 above. In accounting for the observed protective effect, it should be noted that the extracts comprise mixture of organic and resinous matter (Table 5) some of which have good corrosion inhibiting abilities. The complex chemical compositions make it rather difficult to assign the inhibiting action to a particular constituent or group of constituents. Nevertheless, the net adsorption of the extract organic matter on the metal surface creates a barrier to charge and mass transfer, thus protecting the alloy surface from corrodent attack. The degree of protection varies for different extracts, with notable sensitivity to the inhibitor concentration. From Table 5, we observed some similarities in the phytochemical components of the extracts, particularly tannins, alkaloids, and essential oil. The inhibitive properties of tannins has been attributed to the reaction of the polyphenolic fraction of the tannins moieties, which ensures effective protection of the metal surfaces. The triterpenoid and other constituents also posses functional groups which are capable of chelating with aluminium ions and thus facilitate strong coordination on the alloy surface 'Oguzie [15]'. Having ascertained the effectiveness of these plant materials in the present study, subsequent studies to enable precise interpretation of the nature and composition of the absorbed inhibitor layer will be achieved from in-depth research of the corrosion morphology and characterization of the active materials in the absorbed layer is envisaged.

Table 5: Major constituents of the studied plants

Plant	Major constituents
Euphorbia hirta	Triterpenoids, alkaloids, tannins, glycosides, sterols, essential oil, flavones, phenols.
Dialum guineense	Saponins, tannins, alkaloids, flavonoids, essential oil.

(Okwu et al, 2003 i Wikipedia)

Langmuir Adsorption Isotherms

Further elucidation of adsorption mechanism from the experimental data requires estimation of the adsorption modes of the inhibiting species (whether molecular or ionic). The predominant adsorption mode will be dependent on factors such as the extract composition, chemical changes to the extract and the nature of the surface charge on metal. A negative surface charge will favour the adsorption of cations whereas anion adsorption is favoured by a positive surface charge. The plot of the ratio of concentration to surface coverage (C/θ) against concentration (C) displayed a straight line for tested inhibitor (Fig. 3 and 4). Table 1 shows the correlation coefficient of the Langmuir adsorption isotherm. The linear plot with high correlation coefficient (0.999) and slope of about unity (1.10) clearly reveals that the surface adsorption process of Euphorbia hirta and Dialum guineense on the aluminium alloy surface obey the Langmuir adsorption isotherm. Therefore, one can infer that physisorption occurred.

Temkin Adsorption Isotherms

Temkin adsorption isotherm assumes a uniform distribution of adsorption energy, which decreases with the increase of the value of surface coverage, θ . The Temkin adsorption isotherm which favour chemisorption was investigated. Figures 5 and 6 above shows a straight line with a high correlation coefficient. The free energy of adsorption, ΔG_{ads}° , of -48.86 and -138.34 kJmol⁻¹ were obtained for Euphorbia hirta and Dialum guineense extracts respectively. The values obtained agrees with literature survey which suggests chemisorption 'Umoren et al [16]', 'Ebenso et al [17]', 'Obot et al [18]', 'Nnanna et al [19]'.

Effect of Temperature

Two main types of interaction often describe adsorption of organic inhibitors on a corroding system viz: chemical adsorption and physical adsorption. It has been suggested that physisorbed molecules are attached to the metal at the cathodes and

essentially retard metal dissolution by stifling the cathodic reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached 'Ahlberg et al [20], Oguzie [15]'.

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

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad 3$$

whereas estimates of the heats of adsorption (Q_{ads}) were obtained from the trend of surface coverage with temperature as follows 'Bhajiwala [21]':

$$Q_{ads} = 2.303 R \left[\log \left(\frac{\theta_2}{1 - \theta_2} \right) - \log \left(\frac{\theta_1}{1 - \theta_1} \right) \right] \times \frac{T_1 T_2}{T_2 - T_1} \quad 4$$

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.

$$K = \frac{1}{55.5} \exp \left(\frac{-\Delta G_{ads}^\circ}{RT} \right) \quad 5$$

The standard free energy of adsorption, ΔG_{ads}° , which can characterize the interaction of adsorption molecules and metal surface, was calculated by Equation 5. The negative values of ΔG_{ads}° ensure the spontaneity of adsorption process and stability of the adsorbed layer on the aluminium surface. Generally, the values of ΔG_{ads}° around -20kJ/mol or lower are consistent with physisorption, while those around -40kJ/mol or higher involve chemisorptions 'Ebenso et al [22], Oguzie et al [23], Popova [24]'. The values of free energy, ΔG_{ads}° , obtained from the Langmuir isotherm plot are -20.45kJmol^{-1} and -24.04kJmol^{-1} for *Euphorbia hirta* and *Dialium guineense* respectively which is consistent with literature survey and therefore authenticates physical adsorption, and the values of free energy, ΔG_{ads}° , obtained from the Temkin isotherm plot are -48.86kJmol^{-1} and -138.34kJmol^{-1} for *Euphorbia hirta* and *Dialium guineense* respectively which is consistent with literature survey and therefore authenticates chemisorption. This implies that the plant extracts functioned via mixed inhibition mechanism.

Conclusion

Adsorption characteristics of the plant extracts were approximated by the Langmuir and Temkin isotherms. The inhibition mechanism, estimated from the temperature dependence of inhibition efficiency as well as activation parameters show that the extract exhibited mixed inhibition mechanism. Therefore, the Langmuir and Temkin isotherms were obeyed which authenticates the physisorbed and chemisorbed adsorption mechanism.

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