

CORROSION INHIBITION PROPERTIES OF TELFAIRA OCCIDENTALIS LEAF EXTRACT ON ALUMINIUM IN 1.5M HCL MEDIUM

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Abstract: -

Corrosion inhibition of aluminium by leaf extract *Telfaira occidentalis* in 1.5 M HCl was investigated using the gasometric technique at 28°C. Results obtained showed that the extract displayed high inhibition efficiency against corrosion of aluminium in 1.5 M HCl solution. The extract displayed nearly the inhibition efficiencies at concentration range 10 – 50% dilution of the extract. The corrosion inhibition mechanism followed Langmuir adsorption isotherm at the studied temperature. This suggests the extract constituent chemisorbed on the aluminium surface forming a protective film minimising direct contact with the corrodent.

Keywords: *Telfaira occidentalis*, Aluminium, induction time, corrosion inhibition, Langmuir adsorption isotherm.



INTRODUCTION

Through photosynthesis plants harvest solar energy as stored primary metabolites which serve as food for man and animal. Plants also produce secondary metabolites that they used as defence weapon against foreign attack and for adapting during adverse climatic conditions. Vaishnay and Demain 2011, Rogerio *et al* 2010. The secondary metabolites are known as phytochemicals. There are many ethnopharmacological applications of phytochemicals for curing ailments. Chengaiah *et al* 2013. The use of phytochemicals usually obtained in form of extracts or concoctions as therapeutic agents dates back to many human civilisations to the present time. Saxena *et al* 2013. The phytochemicals also have applications in the dye and leather industries. Gohari *et al* 2013, Falcao *et al* 2009. In recent times, plants phytochemicals are also finding applications as corrosion inhibitors Vaishnay and Demain *et al* 2011.

Synthetic organic such as Pyrazolo[3,4-b] pyridine. Rogerio *et al* 2010. Schiff bases of ethylenediamine. Chengaiah *et al* 2013, Quinolines Saxena *et al* 2013, Pyridoxal and Pyridoxol hydrochlorides Gohari *et al* 2013, etc, have been investigated as corrosion inhibitors. These compounds are contain heteroatom by which they chemisorbed on metal surface they constituting a protective coating film that prevents or minimise direct the corrodents Falcao *et al* 2009, Agrawal *et al* 2004. However, there have been concerns for both human health and local ecosystem about the toxicity of these synthetic organic compounds. Hence, there are extensive investigations on green corrosion inhibitors in recent times. Plants phytochemicals are bioactive heterocyclic organic compounds which range from alkaloids, tannins, saponins, steroids, terpenoids, flavonoids, etc. In addition to being biodegradable and less toxic than synthetic corrosion inhibitors, presence of heteroatoms and conjugated bonds in plant phytochemicals impacts on them ability to function as corrosion inhibitors, and a sustainable and inexpensive green corrosion inhibitors.

Although aluminium has high electronegative potential (-1.67 V), it has high resistant to general corrosion due to the formation of a protective surface oxide film. Ebenso *et al* 2010. This resistance is due to the inert and protective character of the Aluminium oxide film which forms on the metal surface. The durability of Aluminium enables its use in many applications and in doing so it may come into contact with aggressive environments. However corrodes rapidly in aggressive corrosion media such HCl solution. *Telfaira occidentalis* is a tropical vine that grows in West Africa. The leaves and the young shoots are the mainly eaten as vegetables Burkill 1985, Nyananyo 2006 2013. Leaves of *Telfaira occidentalis* have been shown to rich in proteins, flavonoid, saponins, phenolic etc Falcao *et al* 2009. These phytochemicals indicates that *Telfaira occidentalis* leaf extracts have potentials as green corrosion inhibitor. However, there is scanty report on corrosion inhibition properties of extracts from *Telfaira occidentalis*. It is therefore of interest to investigated corrosion inhibition properties of methanolic extracts of the leaf of *Telfaira occidentalis* on aluminium.

Materials and method

A 1 mm aluminium sheet was cut into coupons of 24 × 14 mm. The coupons were degreased in absolute ethanol and washed in acetone and then dried in a desiccator. James *et al* 2011. Elemental composition of the aluminium sheet as analysed using Metal Spectrometer Analyser of Model ARL Quanbo Desk OTD 226 (Optical emission) is shown in Table 1.

Table 1: Elemental composition of the Aluminium coupon

Element	Al	Si	Fe	Mg	Zn	Ni	Ti	Cd	Cu	B	Mn
wt %	99.10	0.176	0.60	0.0021	< 0.001	0.0027	0.025	0.0015	0.093	0.0055	0.015

Leaves of *Telfaira accidentails* were air dried and ground into powder. The powder (100 g) was weighed into 1L of 90% methanol in a 2L volumetric flask. The flask was properly corked and left to stand for 48 hours with occasional shaking. The resultant mixture was filtered and the methanol was evaporated to obtain dark brown thick slurry at 65°C using rotatory evaporator. The 50ml crude extract was made up to 1L stock solution with 1.5 M Hydrochloric Acid solution. 50ml of stock solutions diluted with 450ml of 1.5 M Hydrochloric acid solution (10% solution), subsequent dilutions were made with 1.5M HCl solution thus 100ml of stock solution diluted with 400ml (20% solution), 150ml diluted with 350ml (30% solution), 200ml diluted with 300ml (40% solution) and 250ml diluted with 250ml (50% solution). All reagents were analar grade (BDH) and distilled water was used for the preparation of all solutions. The leave extraction Yield of *Telfaira occidentalis* was 4.67%, this is comparable with the 4.2% Extract Yield obtained by Safia *et al*; 2013 in the methanolic extraction of *Raphanus sativus* Schematic diagram of the gasometric (gas-volumetric) technique is shown in figure 1. Detail procedure of gasometric determination of corrosion rates have been described elsewhere. Ehteram and Al Moubaraki 2008. 60ml of the corrosion medium (hydrochloric acid solution only as control) was placed in a Mylius cell. Degreased and weighed aluminium coupon was introduced into the corrodent. Volume of hydrogen gas evolved was collected and measured with the aid of a calibrated tube by downward displacement of water. The readings of H₂ evolved were taken at intervals 1 minutes for minimum of 10 minutes. This procedure was repeated for the corrodent containing varied amount of the *Telfaira occidentails* extract. At the end of each gasometric experiment, the aluminium alloy specimen was removed from the corrodent solution, washed thoroughly with distilled water followed by acetone and dried in air and weighed.

Madukwe *et al* 2013.

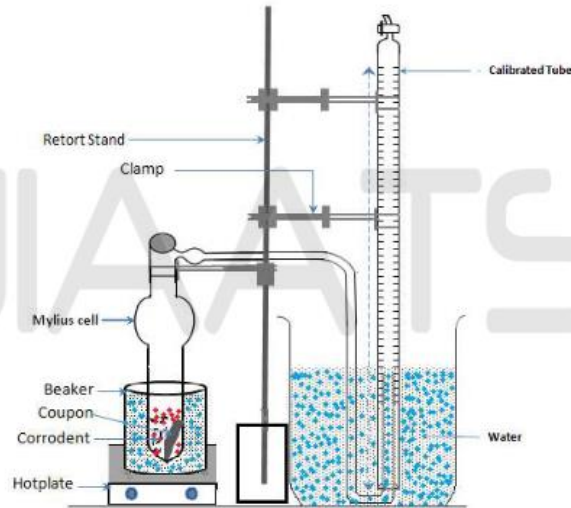


Fig.1 Schematic diagram of the system for the gasometric measurement

The basic data is the volume of hydrogen gas evolved as a function of time. Ehteram and Moubaraki, 2008 . The volume of hydrogen evolved is stoichiometrically proportional to the mass loss in the coupon.

$$\Delta V \propto \Delta W \dots\dots\dots(1)$$

Rate of hydrogen evolution is proportional to rate of mass loss.

$$\frac{\partial \Delta V}{\partial t} \propto \frac{\partial \Delta W}{\partial t} \dots\dots\dots(2)$$

Hence, Corrosion rate = $\frac{\partial \Delta W}{\partial t} = \frac{\partial \Delta V}{\partial t} \dots\dots\dots(3)$

$$= \left(1 - \frac{\text{Corrosion rate}_{\text{with inhibitor}}}{\text{Corrosion rate}_{\text{without inhibitor}}} \right) \times 100 \dots\dots\dots(4)$$

Therefore, inhibition efficiency (IE) =

The surface coverage θ of the inhibitor on the aluminium coupon are calculated from the corrosion rate is given by:

$$\theta = \frac{IE\%}{100} \dots\dots\dots(5)$$

Results and discussion

Hydrogen gas evolution from the aluminium sheet in 1.5 M HCl solution with different concentrations of the inhibitor and without the inhibitor (0%) is presented in Figure 2. For both inhibitor containing and inhibitor free corrodent, there is about 15 minute induction time before hydrogen evolution. This induction time may be attributed to time taken for the corrodent to attacked and remove the protective oxide film on the aluminium sheet coupons. Hence, the readings after 15 minutes represent start of corrosion of the aluminium coupons. After the 15 minutes induction time hydrogen gas evolution increases rapidly from the coupon in the uninhibited corrodent solution. But hydrogen evolutions from the coupons in the inhibited corrodent solutions are very much lowered. The volume of hydrogen gas evolved with time is modelled with four degree polynomials. The expressions for the corrosion rates were obtained by the respective differentials of the hydrogen gas evolved with time. The corrosion rates of the Aluminium sheet coupons in the containing corrodent containing varied concentrations of the inhibitor are shown in Figure 3. The volume of hydrogen evolved is lower in the corrodent containing the inhibitor. This clearly shows that the inhibitor lowered corrosion rate. The corrosion rate decreased very drastically in the presence of the inhibitor. The corrosion rate of the Aluminium coupon increases rapidly with time in the uninhibited corrodent (control). While those in the inhibited corrodent lowered and increase very slowly with time. The extract showed high corrosion inhibition efficiency even at the lowest concentration used in this study.

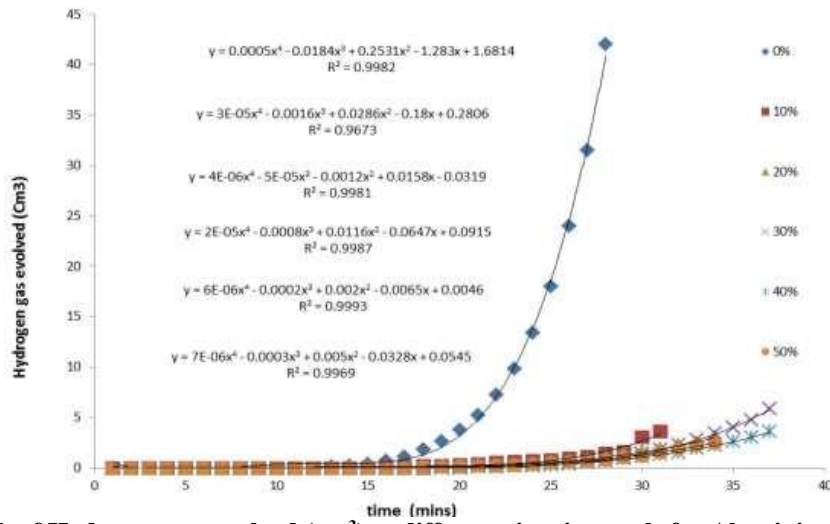


Fig 2: Graph of Hydrogen gas evolved (cm³) at different time intervals for Aluminium corrosion in *Telfaira occidentalis* extracts in 1.5 M HCl at 28 °C

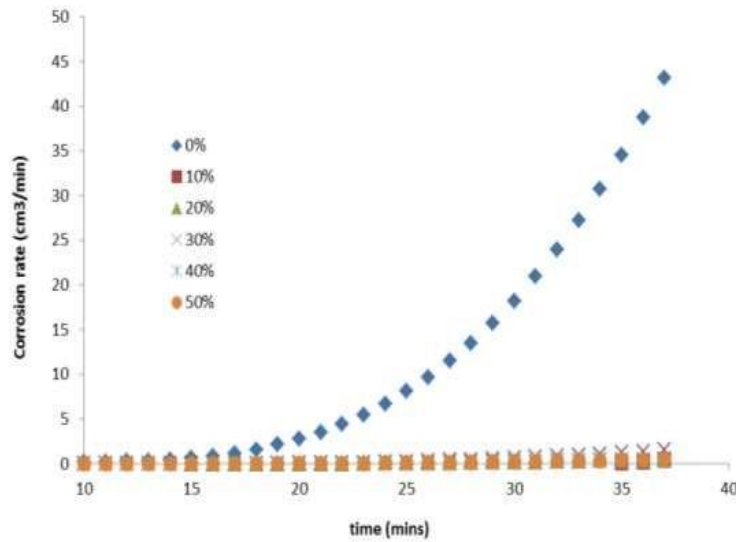


Fig. 3: Graph of Corrosion rate of Aluminium (cm³/minute) against time (minutes) with and without inhibitor (*Telfaira occidentalis* extracts) in 1.5M HCl at 28 °C

Inhibition efficiency as a function of the concentration of the extract depicts a peak at 30% concentration (Fig. 4). This suggests the formation of full protective barrier film of inhibitor molecules on the Aluminium surface.

In Figure 5, Inhibition efficiency as a function of time shows initial passivation due to expected oxide film formed on the metal in an acidic medium. Attack of acid on the metals made the way for manifestations of extract performance. It was more evident on metals in 10% extract where the Inhibition efficiency was at least, the attack was mild on others in various extract concentration especially 30% and 40% extract concentrations

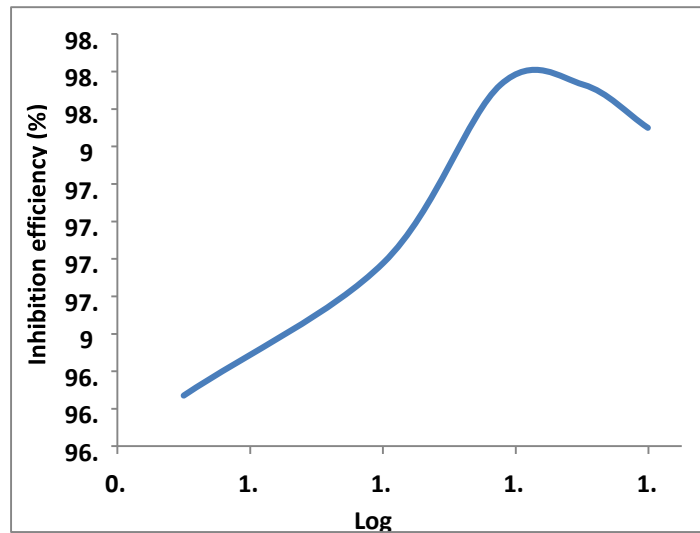


Fig. 4: Relationship between inhibition efficiency and concentration of the extract

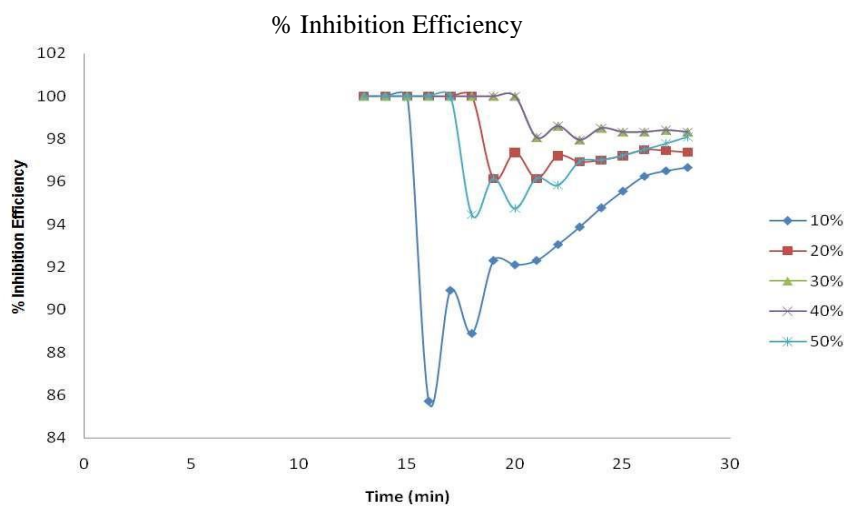


Figure 5; Graph of Inhibition.Efficiency(%) with Time (minutes) for Aluminium corrosion in Telfaira occidentalis extracts in the presence of 1.5MHCl at 28°C

Kinetic Relationship for Corrosion Reactions

The concentration dependence of Corrosion rate can be expressed as indicated below, Mathur *et al* 1982.

$$r = KC^B \dots\dots\dots(6)$$

$$\log r = \log k + B \log C \dots\dots\dots(7)$$

$$\log_{10} r = B \log_{10} C_{\text{extract}} + \log k, \quad y = -0.197x - 8.998$$

Where: $\log r$ (mol/min) = log of corrosion rate

Intercept = $\log k$, k = Specific reaction rate constant, $k = 1.00461579E09 \text{ mol min}^{-1}$

B =Reaction constant (the negative value infer decreasing slope due to the inhibition effect of the extract on the metal) = slope = -0.197 mol^{-1}

C = Volume concentration of extracts (mol)

Corrosion rates can therefore be related to extract concentration by conversion of volume of hydrogen gas evolved in the presence of inhibitor from units of ml (cm^3) to mol assuming hydrogen evolution took place at $1.01325 \times 10^{-5} \text{ Pa}$ Ehteram and Al Moubaraki 2008. In the same vein, a factor of 0.018700307 was employed in converting. Volume of extracts was converted from ml (cm^3) to mol using the factor has been employed in different studies Ajayi *et al.*, 2011; Mathur *et al.*, 1982). From the graph of relationship between $\log r$ and $\log c$ which gave linear expression from where k and B were obtained.

This equation and the previous graph completely depicts the difference between uninhibited and inhibited solutions as the negativity of value obtained in this study compared to that of Ehteram and Al Moubaraki 2008 when no inhibitor was used.

Half-life of the Zinc in the extract

In Figure 6, it was observed that the slope decreases with decrease in reaction rate due to increase in concentration of extract. The larger the magnitude of the intercept, the greater the value of $\log k$ which is solution or reference level of \log

r at extrapolated zero concentration level of a particular extract. A higher intercept represent a higher starting rate of the reaction in a particular extract. Intercept = - 8.998
 Consequently Half Life ($t_{1/2}$) of the metal in the corrosive media in the presence of the extract can be determined by the formula: $t_{1/2} = \ln 2/k$, where $\ln 2 = 0.69314718$, $t_{1/2} = 0.696546601 \times 10^9$ minutes

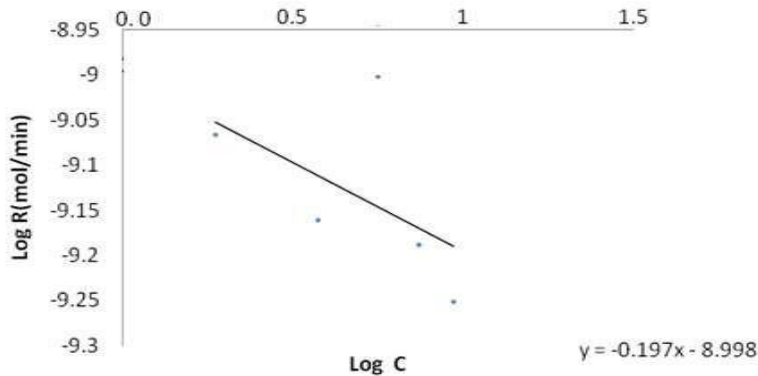


Fig. 6 Graph of Corrosion log r (mol/min) against log of various *Telfaira occidentalis* leave extract concentration C (mole) at 30th minute for Aluminium inhibition in the presence of 1.5MHCl at 28°C

Adsorption studies

Mechanism of corrosion inhibition of the extract may be due to direct interaction of the constituent of the extract with corrodent thereby lowering its effective concentration or by absorbing on the surface of the Aluminium sheet acting as a protective barrier against corrodent attack.

The surface coverage of the inhibitors molecules in the extract on the Aluminium surface agrees with Langmuir adsorption isotherm (Fig. 7). This implies that the film acts as a barrier to acid attack on the Aluminium surface.

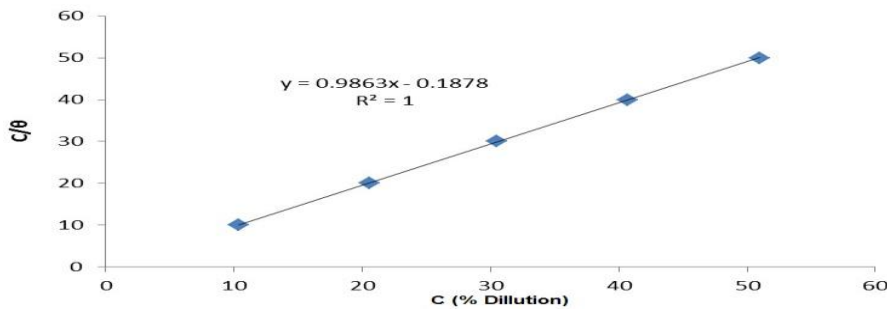


Fig 7: Langmuir adsorption isotherm plot of the extract surface coverage on the Aluminium surface

Langmuir Adsorption Isotherm

This is the most extensively utilised mechanism identical to physical adsorption (physisorption). It is assumed to be of monolayer characteristics by the adsorbate for zero or one adsorbed molecule per site $0 < \theta < 1$, with all sites having the same adsorption energy and no interaction between adsorbed species or adsorption sites. It is represented by the equation:

$$\theta = \frac{kC}{1 + kC} \dots \dots \dots (8)$$

$$\frac{\theta}{\theta - 1} = kC$$

(6) capital k must be changed to small k in this these equations

Dividing both sides $K\theta$ and then rearrange, we then have

$$\frac{C}{\theta} = \frac{1}{k} + C$$

Where θ = Surface coverage

C = Concentration

k = characteristics constant related to adsorption intensity or degree of favourability of adsorption Lebrini et al 2006.

Graph of C/θ (x-axis) against C (y-axis), was discovered to have a slope of 1 and intercept $1/k$, from where k can be simply deduced. Taking log of both sides $\log(C/\theta) = \log C - \log k$ Sheatty et al 2006.

Graph of $\log(C/\theta)$ against $\log C$ give slope to be equal to 1 and intercept $-\log k$. On the other hand $\log \theta / 1 - \theta = \log + y \log C$ Atkins 1994.

Graph of $\log (C/\theta)$ against $\log C$ will give intercept $\log k$ and slope y The equilibrium constant of adsorption $k_{ads} = k^{1/y}$, where $1/y$ is the number of the surface active sites occupied by one inhibitor molecule and C is the bulk concentration of

the inhibitor. Values of $1/y$ less than unity imply the formation of multilayer of the inhibitor on the surface of the metal. However, values of $1/y$ greater than unity indicate that a given inhibitor molecule will occupy more than one active site. For equation $y = 0.9863 x - 0.01878$. Linear graph of Concentration C against C/θ , where θ is the surface coverage of adsorbed material from extract on metal surface. It shows the favourability of adsorption to Langmuir adsorption isotherm. Coefficient of determination $R^2 = 1$ Correlation Coefficient $R = 1$. $1/k = 0.1878$, Therefore characteristic constant $k = 5.32481$.

Gibbs free energy

Adsorption process is ordinarily known to have occurred when free energy value is negative. Therefore by employing the Gibbs Free energy absorption of the extract unto the metal can be calculated Yang *et al.*, (2009).

$$\Delta G = -RT \int_0^a k \frac{da}{a} \dots\dots\dots(9)$$

The above Equation can be represented as

$$\Delta G = -kRT \dots\dots\dots(10)$$

Where: ΔG =Free Energy change

k = Adsorption characteristics constant or degree of adsorption favourability

R =Gas constant

T =Temperature

From Fig: 7, The Gibbs free Energy for this inhibitive reaction can evaluated $\Delta G = -kRT$ $\Delta G = -5.32481 \times 8.314 \text{JK}^{-1} \text{mol}^{-1} \times 301\text{K}$, the negative value of ΔG ($-13,319.00 \text{Jmol}^{-1}$.) It is an indication of spontaneous physical adsorption.

Morphological Analysis

It could be observed that the grains in the internal structure in Plate 2.0 were highly attacked by the 1.5 M HCl in the absence of leave extract compared with the control in Plate 1.0 not immersed in acid or extract. In that Plate 2.0 there were much depletion of α -Aluminium phase into the corrodent due to corrosive effect of the medium on the metal. This however had less effect on Al-Si and Al-Fe phases present in the sample in Plate 2, they therefore remained prominent in the structure as much of the major phase α -Al got dissolved in to the solution In Plate 3.0, the structure of Aluminum sample immersed in leave extract indicated that the internal structure was protected, because less of α -Al phase dissolved into the solution containing the *Telfaira occidentalis* extract in acidic medium due to inhibitory effect of phytoconstituents in the extract..

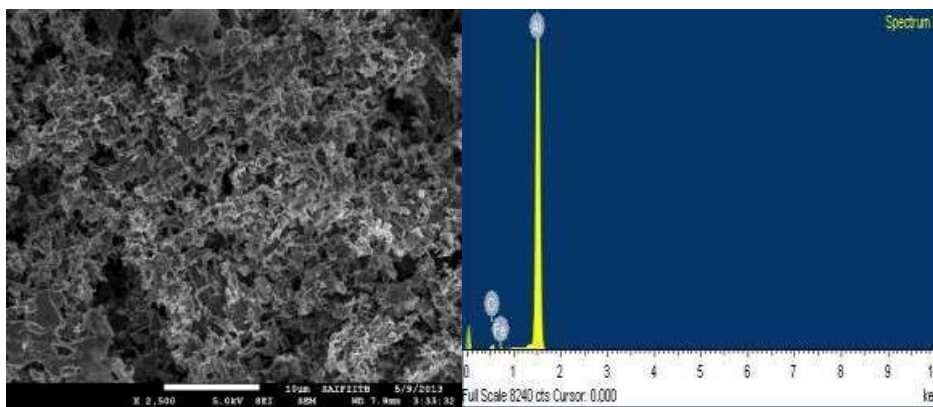


Plate 1.0A (a) SEM IMAGE of Aluminium as received (b) EDX SPECTRUM of Aluminium as received

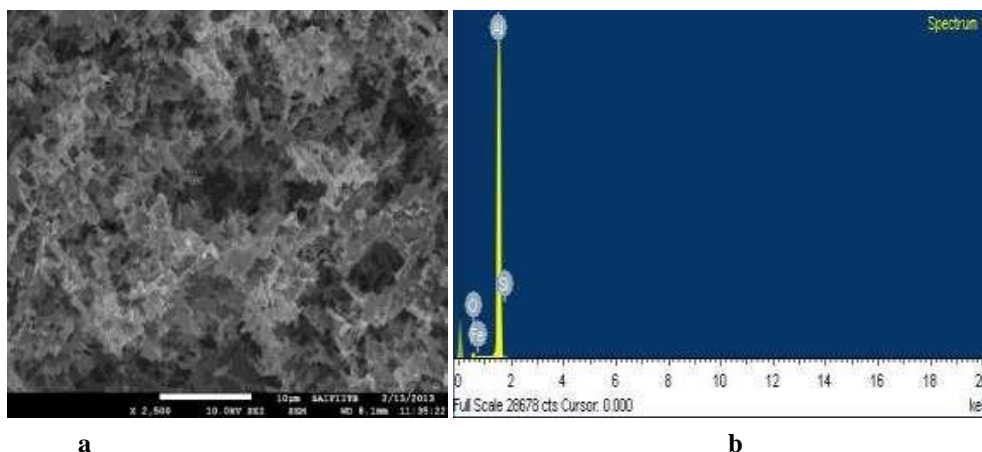
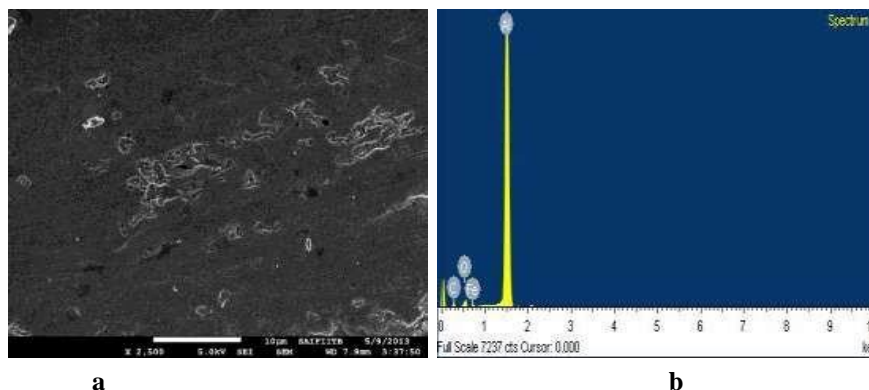


Plate 2.0A(a) SEM IMAGE of Corroded Aluminium in 1.5 M HCl(Control), (b) EDX Spectrum of Corroded Aluminium in 1.5 M HCl(Control)



**Plate 3.0A (a) SEM IMAGE of Aluminium in *Telfaira occidentalis* extract
(b) EDX spectrum of Aluminium in *Telfaira occidentalis* extract**

Conclusions

Methanolic extract of leaf of *Telfaira occidentalis* in 1.5M HCl was investigated as green corrosion inhibitor for aluminium using the gasometric technique at 28°C. There was about fifteen minute's induction period before the susceptibility of the aluminium sample to corrosion in the HCl media. This initial resistance to corrosion is due to strongly adhered oxide film on the aluminium surface. Removal of the oxide film by aggressive chloride ion in the medium took fifteen minutes before the aluminium surface is accessible for adsorption by the secondary metabolites in the extract. The protected aluminium surface by the extract against acid attack was observed in the SEM analysis. The deduced long Half life of $t_{1/2} = 0.696546601 \times 10^9$ minutes depicts high retardation in corrosion reaction. The phytochemicals in the extract displayed high corrosion inhibition efficiency and the inhibition mechanism is explained by Langmuir adsorption isotherm having ΔG (-13,319.00 Jmol⁻¹.) which is an indication of spontaneous physical adsorption. This investigation proofed that TO be effective corrosion inhibitor by reducing the volume of hydrogen gas discharged from aluminium as well as slow down of the corrosion rate in the presence of acid environment.

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