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Electrochemical Analysis of *Piliostigma thonningii* (Monkey Bread) Leaf Extract as Corrosion Inhibitor of Aluminium in Alkaline Medium

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ARTICLE DETAILS

ABSTRACT

Inhibition of aluminium corrosion in alkaline environment by *Piliostigma thonningii* at 303, 313 and 323 K was studied using gravimetric and electrochemical measurements. The weight loss and electrochemical data used for further calculation of some corrosion parameters. The percent inhibition efficiency (%I_E) increased with concentration of *P. thonningii*. Temperature increased the corrosion rate but decreased the inhibition efficiency between 303, 313 and 323 K in the absence and presence of the inhibition respectively. Physical adsorption was proposed from Ea values obtained. The increase in the percent inhibition efficiency as well as the surface coverage (θ) indicated that the adsorption of *P. thonningii* on the reaction sites of NaOH plays an important role in the adsorption process. Adsorption isotherms were fitted by Langmuir isotherm. The electrochemical results indicated that the investigated compound acts as mixed – type inhibitor. Some thermodynamic parameters were also determined to investigate the mechanism of corrosion inhibition (G^oads) and kinetic parameters were evaluated. The presence of – C =O and –N=N-, etc., groups in *P. thonningii* was found to have contributed greatly to the inhibition process by interacting with aluminium surface.

1. Introduction

Corrosion of metals is one of the most significant problems faced by advanced industrial societies. Although corrosion is a serious problem for many metals, corrosion can be pictured as short circuited galvanic cells in which some regions of the metals surface acts as cathode and other as anode and electric circuit is completed by electron flow through the iron itself. This electrochemical cells form in parts of the metal where there are impurities or regions that are subject to stress [1].

In most cases, corrosion involves two related chemical reactions such as-oxidation and reduction. In oxidation, the atoms of a metal give up electrons to a liquid or a gas. In reduction, part of the same metal or adjoining metal captures these electrons from the liquid or gas. Electrons flow from one part of a metal to other to form an electric circuit. In this sense, corrosion is an electrochemical process [1].

There are various types of corrosion. One kind, called localized attack, occur on small areas of bare metal and produces holes or cracks. Another type, uniform corrosion, attacks many areas, such as the surface of an aluminium pot or copper roof. On copper roofs, for example, such corrosion produces a thin, greenish film called patina that protects the surface against further rapid corrosion [2].

The type of corrosion and its severity depend on the chemical makeup of and the corrosive agent. Other major factors include stresses in the metal, the temperature of the corrosive agent, and the speed at which the agent moves against the metal. Corrosion tend to be more severe if the agent contains solid particles, the corrosion is even worse and is called erosion corrosion [2]. Corrosion can also occur on materials other than metals, such as ceramics or polymers, although in this context, the term degradation is more common. Corrosion degrades the useful properties of materials and structure including strength, appearance and permeability to liquids and gases. Many structural alloys corrode merely from exposure to moisture like in air, but the process can be strongly affected by exposure to certain substance. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion controlled process, it occurs on exposed surfaces [3].

Aluminium is remarkable for the metal's low density and for its ability to resist corrosion due to the phenomenon of passivation. Structural components made from aluminium and its alloys are vital to the aerospace industry and are important in other areas of transportation and structural materials. Corrosion can be reduced due to a thin surface layer of aluminium oxide that forms when the metal is exposed to air, effectively preventing further oxidation. The strongest aluminium alloys are less corrosion resistant due to galvanic reaction with alloyed copper. Aluminium is one of the few metals that retain silvery reflectance in finely powdered form, making it an important component of silver coloured paint [3]. The aim of the study is to evaluate the inhibitory characteristics of *Piliostigma thonningii* extracts on aluminium corrosion.

2. Experimental Methods

2.1 Sample Collection and Material Preparation

The aluminium sheet specimen was obtained from Mubi market, Adamawa State. The aluminium sheets specimens were mechanically cut into coupons of dimension 5 cm x 4 cm and the thickness of 0.19 cm respectively with a hole drilled at one end for free suspension. The specimens were used without further polishing to ensure reproducible surface. The coupons were degreased in ethanol, dried in propanone and stored in moisture-free desiccators before the study commenced [4].

Fresh leaves of *Piliostigma thonningii*, PT was collected, dried and pulverized into powder form. The materials were dried in shade to enrich the active ingredients in them by reducing their moisture content. 50 mg each of the fine powdered sample was dissolved in 100 mL methanol in a beaker for the extraction. The methanolic extracts were concentrated on an evaporator (RYC-R-205D) at 45 °C before decantation and filtration [4].

2.2 Gravimetric Measurements

The procedure reported earlier by Onen *et al*., [5] collaborated by Eddy *et al*., [6] was adopted for gravimetric measurements.

%I_E= (M$_0$-M$_1$/M$_0$) x 100

θ =[1-M$_1$/M$_0$]

CR (mgh^{-1} cm^{-2}) = M/DAT

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where %I is the percent inhibition efficiency, θ is the surface coverage, CR is the corrosion rates Mo and M_1 are the weight loss in the absence and presence of the inhibitor, D is the density of the metal, A is the surface area of the metal and T is the immersion time.

2.3 Electrochemical Measurements

The electrochemical experiments were carried out using a three electrode cells having aluminium as working electrode, potassium chloride as reference electrode and platinum electrode as counter electrode. The metal surfaces were polished well with silicon carbide paper before use. The alkaline solution was used as electrolyte with different concentrations of inhibitor at 303 K, 313 K and 323 K. Potentiodynamic polarization study was conducted and the inhibition efficiencies of the inhibitors were calculated [7]. For polarization curves, the working electrode was immersed in a test solution for 30 min until a steady state open circuit potential (Eocp) was obtained. The polarization curve was recorded with a scan rate of 100 mVs^{-1} [8].

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

A small quantity of powder sample was exposed to infrared radiation. The sample molecules selectively absorb radiation of specific wavelengths which causes the change of dipole moment of sample molecules. Consequently, the vibrational energy levels of sample molecule transferred from ground state to excited state. The frequency of the absorption peak was determined by the vibrational energy gap. The intensity of absorption peak was related to the change of dipole moment and the possibility of the transition of energy levels. The common use region for infrared absorption spectroscopy was 4000 – 400 cm^{-1} because the absorption radiation of most organic compounds and inorganic ion was within this region [9].

3. Results and Discussion

3.1 Effect of Corrodent Concentration and Temperature on Aluminium Corrosion

Fig. 1 and Table 1 show the variation of weight loss with time (days) for aluminium corrosion in NaOH at 303 K, 313 K and 323 K with *Piliostigma thonningii* (PT).

The results show that the weight loss of aluminium in NaOH increased with increasing alkaline concentration and temperature. Similar trends were observed at all given temperature (K) with higher weight loss. This could be attributed on an increase in the rates of ionization and diffusion of active species in the corrosion process. In addition, rates of chemical reaction increase with increasing alkaline concentration and temperature. Similar observation has been made by various workers on the corrosion of metals in H₂SO₄ and HCl solutions [10, 11].

Table 1 Corrosion parameters of aluminium corrosion in 0.10 M NaOH containing PT from weight loss measurement

| Inhib. Conc. (mg dm^{-3})	Weight loss (mg)			Corros. Rate (mdd)x10^{-5}			Inhibition Efficiency (%I$_E$)			Surface Coverage (θ)		
	303	313	323 K	303	313	323 K	303	313	323 K	303	313	323 K
Blank	0.194	0.262	0.552	5.45	6.18	7.12	-	-	-	-	-	-
PT												
10	0.665	0.699	0.876	5.20	5.87	6.56	93.43	85.51	81.72	0.93	0.86	0.82
30	0.622	0.643	0.834	4.79	5.57	6.43	94.53	88.66	97.14	0.95	0.89	0.87
50	0.598	0.612	0.801	3.87	4.86	5.20	96.55	92.50	90.32	0.96	0.93	0.90
70	0.467	0.589	0.762	3.53	3.98	4.45	98.32	96.11	93.57	0.98	0.96	0.94
100	0.410	0.523	0.716	2.97	3.64	4.32	98.73	97.97	94.49	0.99	0.98	0.95
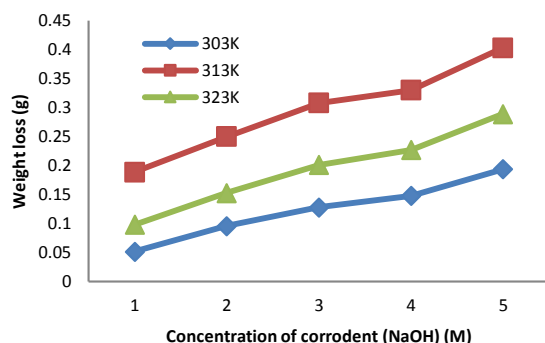
Fig. 1 Plot of weight loss, A$_1$, with time, t (days) for aluminium corrosion in difference concentration of NaOH at 303 K, 313 K and 323 K
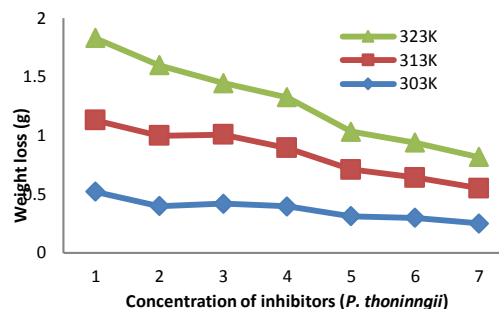

Fig. 2 Plot of weight loss, M$_1$, with time, t (days) for aluminium corrosion in 0.10 M NaOH with various concentration of PT at 303 K, 313 K and 323 K

3.2 Effect of Inhibitor (Piliostigma thonningii) Concentration on Aluminium Corrosion

Figs. 1 and 2 show the variation of weight loss with time (days) for aluminium corrosion in 0.10 M NaOH with various concentration *of Piliostigma thonningii* at 303 K, 313 K and 323 K but with lower weight loss. The plot reveals that the weight loss was lowest at 100 mgdm^{-3} (highest concentration of inhibitors studied) on aluminium. This indicate that the inhibitors *Piliostigma thonningii* actually inhibited the corrosion of aluminium with inhibition increasing with inhibitor concentration and decreases with increasing in temperature.

Table 1, reflect the values of weight loss of corrosion rate, inhibition efficiency and surface coverage for aluminium corrosion in 0.10 M NaOH with *Piliostigma thonningii* and blank. The corrosion rate was more in the blank at 303 K. Similar trend was observed at 313 K and 323 K but with higher values of corrosion rate. With addition of the inhibitor (PT extracts), corrosion rates decreased while the inhibition efficiency and surface coverage decrease with increasing temperature (303 – 323 K) with maximum at 303, 313 and 323 K respectively (95.43%, 93.51%, 90.72%). This shows that the inhibitors, PT function at lower temperatures. The decrease in inhibition efficiency with increasing temperature shows that the time fall for the adsorption of PT molecules on aluminium shorter. This assertion agrees with the findings of Ebenso et al. [12] and Onen and Nwufo [13]. The behaviour of the inhibitors at 303 K may be attributed to the adsorption of the inhibitors up to 313 – 323 K and after the further increase in temperature brings about desorption of the inhibitors, PT under study. This shows that adsorption and desorption of the inhibitor molecules continuously occur at metal/alloy surface and equilibrium exists between the process at certain temperature with increase in temperature, the equilibrium between adsorption and desorption process is shifted leading to higher desorption rate than adsorption unless equilibrium is established at a different value of equilibrium constant. This shows that lower inhibition efficiencies at higher temperature. This assertion is in agreement with studies by Nalini et al., [14], he found out that at high temperature the inhibition efficiency is low, while at low temperature the inhibition efficiency is high.
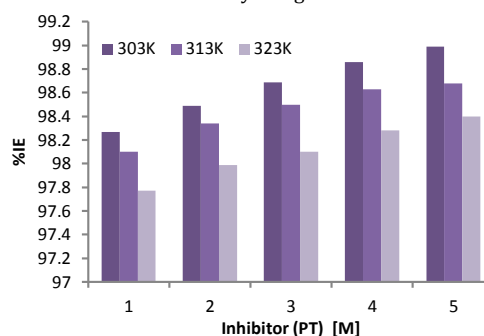

Fig. 3 Plot of %I$_E$ versus inhibitor (PT) concentration [M] for aluminium corrosion at 303 K, 313 K and 323 K

Table 2 Kinetic and thermodynamic data for aluminium corrosion in 0.10 M NaOH containing PT from weight loss measurements

Inhibitor Conc. (mgdm^{-3})	Activation energy, Ea (kJmol^{-1})	Heat of Adsorption, Qads (kJmol^{-1})
Blank	12.57	-
PT		
10	5.53	-5.43
30	5.85	-5.82
50	5.99	-5.92
70	6.34	-6.81
100	6.78	-8.41
Mean	6.10	-6.48

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3.3 Kinetic and Thermodynamic Consideration

Table 2 shows the calculated values of activation energy, Ea for PT extract studied, with a mean of 6.10 kJmol^{-1}, is lower than 40 kJmol^{-1} indicating that the compounds are physically adsorbed on aluminium surface. Physical adsorption requires that the average Ea to be 40 kJmol^{-1} and inhibition efficiency should increase at lower temperatures. This agrees with earlier made by Onen et al., [10].

The activation energy calculated values presented in Table 2 were obtained from the plots of logarithm of rates constant (k) against the inverse of temperature under study 303, 313 and 323 K. The slope of the line multiple by the ideal gas equation R gives the activation energy Ea. The activation energy of the inhibited solution decrease by increasing the concentration of the inhibitor: *Piliostigma thonningii* .These findings show that this inhibitors retard the corrosion of aluminium in the studied media (NaOH).

3.4 Adsorption Consideration

From Table 1, it is evident that the surface coverage and inhibition efficiency increases with increasing inhibitor concentration and decrease with increasing temperature, from 303-323 K. This shows the physical adsorption. This assertion is in good agreement with earlier observations made [10-12]. He observed that the inhibitors concentration affect inhibition efficiency, the higher the concentration the higher the inhibition efficiency and the higher the temperature the lower the inhibition efficiency. Fig. 4 shows plots of adsorption isotherms of PT at 303 K, 313 K and 323 K. This further confirms physisorption for the inhibition process.

The high surface coverage data observed at high inhibitor concentration is due to very strong interactions between the adsorbed species. This surface coverage data implies that the adsorption of PT extracts at aluminium interface may be due to electrostatic force between the atoms on the metal surface and adsorbates. This observation agrees with earlier assertion made by various workers [10, 14-16].
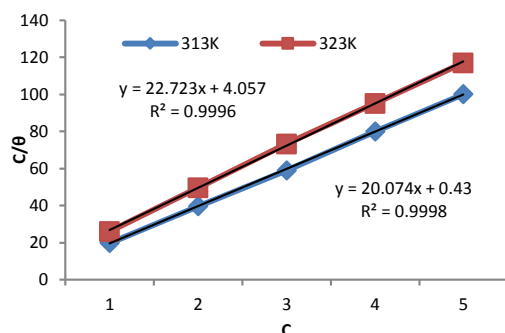

Fig. 4 Langmuir adsorption isotherm plotted as C/θ versus C for aluminium corrosion containing PT at 303 K, 313 K and 323 K

Table 3 Data obtained from potentiodynamic polarization curves aluminium electrode in 0.1 M NaOH in different concentrations of the extracts at 303 K

	Inhibitor Conc. (mgdm^{-3})	-E$_{corr}$ (vs KCl EV^{-1})	I$_{corr}$ (10^{-8} JAcm^2)	-β$_c$ (mV dec^{-1})	β$_a$ (mV dec^{-1})	η$_p$ (%)
Blank	0.00	0.519	17.00	0.636	0.519	-
P. thoninngii	10.00	1.014	9.509	1.036	1.012	94.23
	30.00	0.994	8.679	1.028	0.993	95.63
	50.00	0.690	8.081	0.789	0.689	97.55
	70.00	0.667	7.129	0.733	0.659	98.72
	100.00	0.590	5.447	0.674	0.599	99.06

The potentiodynamic polarization curves of aluminium in 0.1 M NaOH solution in the absence and presence *Piliostigma thonningii* (PT). The values of related electrochemical parameters i.e., corrosion potential (E$_{corr}$), corrosion current density (i$_{corr}$), cathodic Tafel slope (bc) and inhibition efficiency ηp were calculated. The *ηp* was calculated from polarization measurements according to the relation given below,

$$\eta_p = \left[\frac{i_{corr}(un_{inh}) - i_{corr}(inh)}{i_{corr}(un_{inh})} \right] \times 100$$

where i$_{corr}$ (un$_{inh}$) and i$_{corr}$(inh) are uninhibited and inhibited corrosion current respectively. Corrosion currents were obtained by the extrapolation of the current potential lines to the corresponding corrosion potentials (Table 3 and Fig. 5) [8].
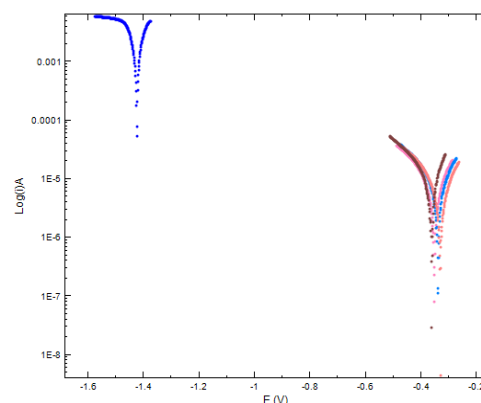

Fig. 5 Potentiodynamic linear polarization curves for aluminium in 0.1 M NaOH without and with different concentrations of PT at 303, 313 and 323 K (immersion time 2 minutes)
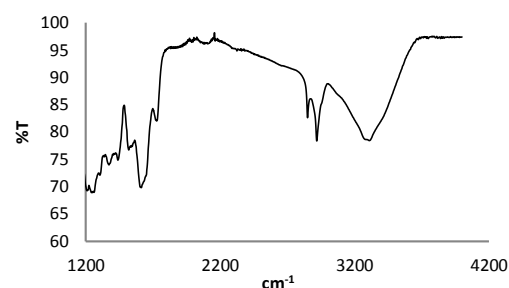

Fig. 6 FT-IR transmittance spectra of *Piliostigma thoninngii*

3.5. FT-IR Analysis of Piliostigma thonningii Extract

Transmission vibrational spectrum of *Piliostigma thonningii* is shown in Fig. 6. An absorption band is observed at 3200 cm^{-1} for the sample. This indicates the presence of a terminal alkyne. At 3020 cm^{-1}, an hydroxyl group overlapped by the strong stretching mode of O-H is found to be present. It is also indicative of N-H and C-H stretching bands. At 2200 or 2190 cm^{-1} is related to C≡C and C≡N strong stretching vibration. The C-F, C-N and C-O absorption bands at 1440 cm^{-1} observed for PT could be due to strong stretching of alkyl halide; medium stretching in amine; and strong stretching in acid. There are also some absorption bands at 1033 or 1029 cm^{-1}, which can be ascribed to C-F or C-O stretching vibration for *Piliostigma thonningii* [17].

4. Conclusion

This plant extract, *Piliostigma thonningii* studied as an inhibitor retarded alkaline corrosion of aluminium to an appreciable extent being physically adsorbed on the metal/alloy surface. The rate of corrosion of aluminium in alkaline solution is a function of the concentration of *Piliostigma thonningii* extracts and temperature dependent. The inhibition efficiency increase with increase in additive concentration and decrease with increase temperature in order: PT, *Piliostigma thonningii,* could be used to replace the toxic inhibitors. From the two isotherms accessed, Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of the investigated compounds at all temperatures studied. The potentiodynamic studies revealed that *Piliostigma thonningii* is a mixed type inhibitors i.e., it affect both cathodic and anodic reactions.

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