Investigation of *Anthocleista djalonensis* Stem Bark Extract as Corrosion Inhibitor for Aluminum.

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ABSTRACT

The inhibitive effect of water extract of the bark of *Anthocleista djalonensis* (WEAD) on acid corrosion of aluminum was investigated using the gravimetric method. The result showed that the inhibition efficiency depended on the concentration of *Anthocleista djalonensis* extract. The inhibition efficiency ranged from 39.76-96.50%. The inhibition efficiency is concentration and time dependent. It increased with concentration and decreased with immersion time. Corrosion penetration rate reached 0.0022 mm/y and decreased to 0.0006 mm/y at 50/50 vv.

(Keywords: aluminum corrosion, Al, penetration rate, inhibition, Anthocleista djalonensis)

INTRODUCTION

Corrosion is a major problem that must be confronted for safety, environmental, and economic reasons [1]. Combining technological progress with environment safety has become a key challenge of the millennium and cleaner technology or production has been identified as an ideal method of reconciling economic development with the safety of the environment.

Large numbers of organic compounds have been studied and are being studied to investigate their inhibitive effect. These studies have shown that organic compounds, especially, those having hetero-atoms (such as N, S and O) in their aromatic or long chain carbon systems show significant inhibition efficiency [2-4]. However, most of these compounds are not just expensive, but also toxic to living things [5]. It is therefore needless to point out the importance of cheap and safe corrosion inhibitors and this has prompted the recent research for green corrosion inhibitors.

Green corrosion inhibitors are biodegradable, and rich sources of ingredients with high inhibition efficiency [6 and 7] environmentally acceptable, readily renewable source for a wide range of inhibitors [8-10] and do not contain heavy metals or toxic compounds [11]. These green inhibitors are non-hazardous, eco-friendly and environmentally acceptable.

The aim of the present work is a follow up on the investigations going on in our corrosion laboratory on inhibitive properties of phytochemical plants: *A. djalonensis, A. vogelii, Nicotina tubaccum, Carica papaya, Capsicum fruitenses*.

EXPERIMENTAL

Preparation of Stem Bark Extract

Samples of *Anthocleista djalonensis* stem bark, was obtained along the Government Reserved Forest (J4), Ijebu North East, Ogun State, South Western Nigeria. Samples of the bark were sun dried for six weeks (6 wks), pulverized and sieved through a mesh 10 sieve. Fifty grams (50 g) of the powdered material was then introduced into a round bottomed flask filled with 1000 ml of distilled water. The mixture was boiled for one hour (1 hr) using water bath and left to stand for 24 hours, then filtered to remove suspending impurities. The aliquot (extract) was used as corrosion inhibitor in the present case.

Preparation of Specimen

Aluminum sheets (3mm thick) with nominal composition 0.8%Si, 0.7%Fe, 0.4%Cu, 1.2%Mg, 0.35%Cr, 0.25%Zn, 0.15%Ti and the rest Al was supplied by Tower Aluminum Plc., Lagos. The sheet was cut into 1.0 ×4.0× 0.2 cm rectangular coupons.

The surfaces of the newly cut coupons were thoroughly polished with emery paper, from lower grade–150, to higher grade–1200, to a mirror like surface. The polished coupons were washed with distilled water, degreased with acetone, wrapped within folds of filter paper and desiccated overnight before weighing.

Mass Loss Method

Aluminum specimens in triplicate were immersed in 100ml of solutions with and without plant extract for a period of 3, 6, 9, 12 and 15 hours respectively. At the end of each period of immersion, the coupons were washed with distilled water, wrapped within folds of filter paper and desiccated over night. The final weights of the coupons were then obtained by weighing. The used coupons were polished again to mirror-like surface, for the new sets of experiments. The weight loss was calculated using the equation:

$$\Delta W = W_1 - W_2 \quad \textbf{(1)}$$

Where W_1 = Initial weight of coupons before immersion

W_2 = Final weight of coupons after immersion

ΔW = Weight loss of coupons.

The percentage inhibition efficiency (%IE) was then calculated from the resulting weight loss data as follows:

$$\%I.E = \left(1 - \frac{w_{Li}}{w_{Lb}}\right) x100 \quad \textbf{(2)}$$

Where W_{Li} = Weight loss of coupons in inhibited solution.

W_{Lb} = Weight loss of coupons in blank/ uninhibited solution.

While the surface coverage θ and the corrosion penetration rates were calculated using Equations (3) and (4), respectively.

$$\theta = \left(1 - \frac{w_{Li}}{w_{Lb}}\right) \quad \textbf{(3)}$$

$$CPR_{mmy^{-1}} = \frac{KW}{\rho AT} \quad \textbf{(4)}$$

Where K, w, ρ, A, T are the conversion factor (87.6), weight loss, density, surface area and time, respectively.

RESULTS AND DISCUSSION

The inhibition efficiency (%IE), the surface coverage (θ), and the corrosion penetration rate (mmy^{-1}) calculated from the weight loss measurement of sulfuric acid and inhibitor *(A. djalonensis*) for the immersion periods of 3, 6, 9, 12 and 15 hours, are given in Tables 1–5.

It is seen from the Tables that WEAD acts as a good inhibitor for corrosion of aluminum in 0.5 M H_2SO_4 for the experimental periods under study. The weight loss decreased with increasing concentration of plant extract.

Table 1: Weight Loss, Inhibition Efficiency Surface Coverage for 3 hrs (30^oC).

	WEIGHT LOSS (g)	INHIBITION EFFICIENCY (%)	CORROSION PENETRATION RATE (mmy^{-1})	SURFACE COVERAGE
0.5M H_2SO_4	0.0014	___	0.0052	-----
INHIBITED 10/10 (V/V)	0.0006	57.12	0.0022	0.5712
20/20	0.0005	64.29	0.0019	0.6429
30/30	0.0004	71.14	0.0015	0.7114
40/40	0.0002	85.71	0.0007	0.8571
50/50	0.0002	85.71	0.0007	0.8571

Table 2: Weight Loss, Inhibition Efficiency and Surface Coverage for 6 hrs at (30˚C).

	WEIGHT LOSS (g)	INHIBITION EFFICIENCY (I%)	CORROSION PENETRATION RATE (mmy-1)	SURFACE COVERAGE
0.5M H_2SO_4	0.0022	___	0.0041	-----
INHIBITED 10/10 (V/V)	0.0009	59.09	0.0017	0.5909
20/20	0.0008	63.63	0.0015	0.6363
30/30	0.0006	72.72	0.0011	0.7272
40/40	0.0004	81.18	0.0007	0.8118
50/50	0.0003	86.36	0.0006	0.8636

Table 3: Weight Loss, Inhibition Efficiency and Surface Coverage for 9 hrs at (30˚C).

	WEIGHT LOSS (g)	INHIBITION EFFICIENCY (I%)	CORROSION PENETRATION RATE (mmy-1)	SURFACE COVERAGE
0.5M H_2SO_4	0.0028	___	0.0035	-----
INHIBITED 10/10 (V/V)	0.0015	53.57	0.0016	O.5357
20/20	0.0012	57.14	0.0015	0.5714
30/30	0.0009	67.86	0.0011	0.6786
40/40	0.0007	75.00	0.0008	0.7500
50/50	0.0005	82.14	0.0006	0.8214

Table 4: Weight Loss, Inhibition Efficiency and Surface Coverage for 12 hrs at (30˚C).

	WEIGHT LOSS (g)	INHIBITION EFFICIENCY (I%)	CORROSION PENETRATION RATE (mmy-1)	SURFACE COVERAGE
0.5M H_2SO_4	0.0035	___	0.0033	------
INHIBITED 10/10 (V/V)	0.0019	47.22	0.0018	0.4722
20/20	0.0017	52.78	0.0016	0.5278
30/30	0.0014	61.11	0.0013	0.6111
40/40	0.0009	75.00	0.0008	0.7500
50/50	0.0007	80.56	0.0005	0.8056

Table 5: Weight Loss, Inhibition Efficiency and Surface Coverage for 15 hrs at (30˚C).

	WEIGHT LOSS (g)	INHIBITION EFFICIENCY (I%)	CORROSION PENETRATION RATE (mmy-1)	SURFACE COVERAGE
0.5M H_2SO_4	0.0043	___	0.0031	------
INHIBITED 10/10 (V/V)	0.0022	47.19	0.0016	0.4719
20/20	0.0019	55.81	0.0014	0.5581
30/30	0.0017	60.47	0.0012	0.6047
40/40	0.0013	72.09	0.0009	0.7209
50/50	0.0010	76.75	0.0007	0.7675

As the concentration of plant extract increases, the percentage inhibition efficiency (%IE) progressively increases from 57.12 – 85.71% at 3 hr immersion period and decreased to 47.22-80.56% at 12 hr immersion period. Even though the inhibition efficiency is time dependent, the immersion time has nominal decrease on the inhibition efficiency.

The corrosion penetration rate decreases with increase in concentration of the WEAD. The surface coverage (θ) is highest for 50/50 vv concentration and reached an optimal level of 86.36%.

Figure 1 shows the plots of weight loss in the presence and absence of inhibitor as a function of concentration. From the figure, the weight loss decreased with concentration and increased with immersion time (Figure 2). Figures 3 and 4 showed the variation of %IE with concentration and corrosion penetration rate with time. From Figure 3, %IE increased with extract concentration while the corrosion penetration rate decreased with time. These observations are indicative that the presence of WEAD 'arrested' metal dissolution in 0.5M H_2SO_4.

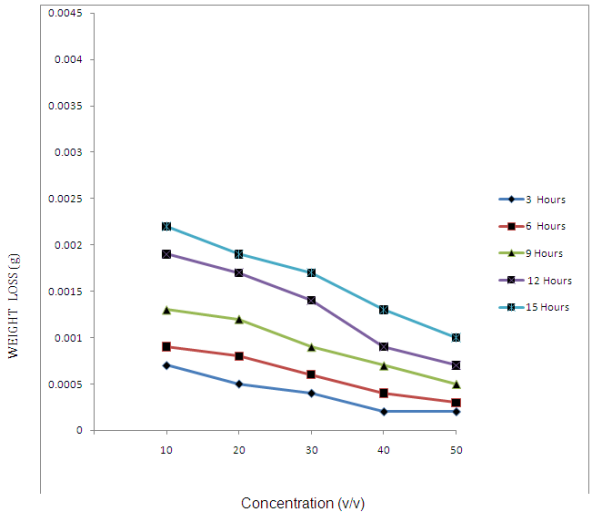


Figure 1: Variation of Weight Loss of Aluminum with the Concentration of *A. djalonensis* Bark Extract.

Anthocleista djalonensis

Anthocleista djalonensis is mainly a native of tropical Africa, Madagascar, and Mascarene Islands [12]. Traditional healers in Sibi in Mali reported that *A. djalonensis* is used frequently in the treatment of malaria and abdominal pain [13], Onocha, *et al.* [14] reported and isolated monoterpene diols, xanthone, dibenzo-alphapyrone-djalonensone from the leaves, stem bark and roots of *A. djalonensis*. The chemical structures of some of these compounds are shown in Structures I – IV.

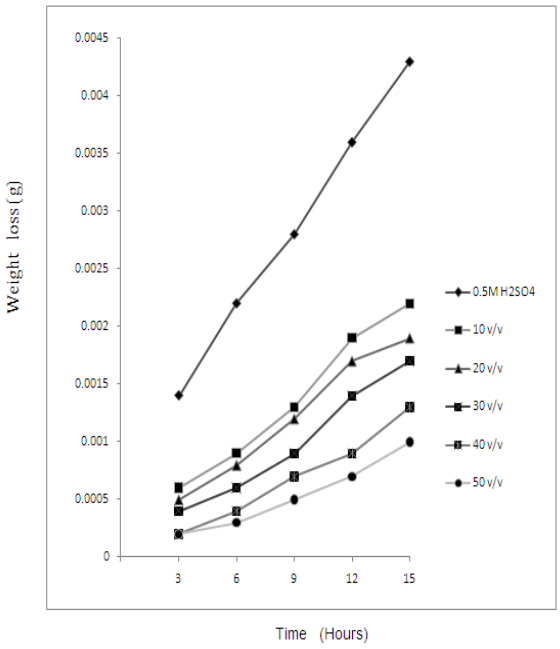


Figure 2: Variation of Weight Loss of Aluminum with time in 0.5M H_2SO_4 in the presence of *A. djalonensis* Bark Extract.

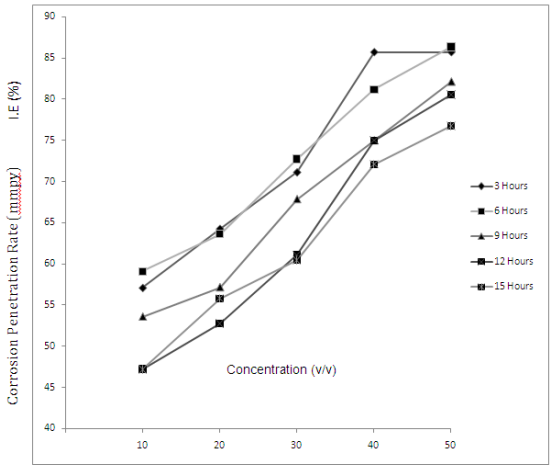


Figure 3: Variation of Inhibition Efficiency of *A. djalonensis* Bark Extract with Concentration.

Inspection of Structures I – IV reveals that the compounds contain multifunctional groups and they are strongly adsorbed on the metal surface. The adsorption of these compounds on the metal surface make a barrier for mass and charge transfer.

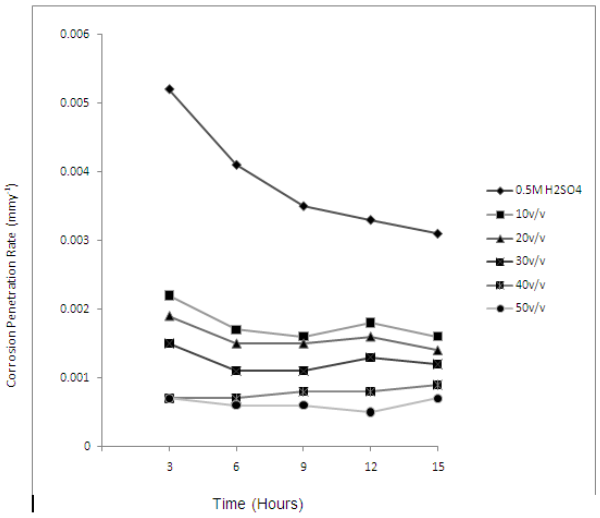
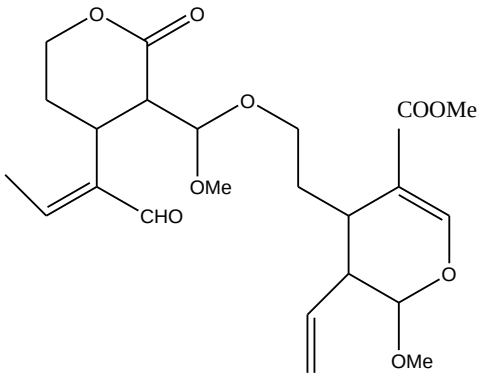
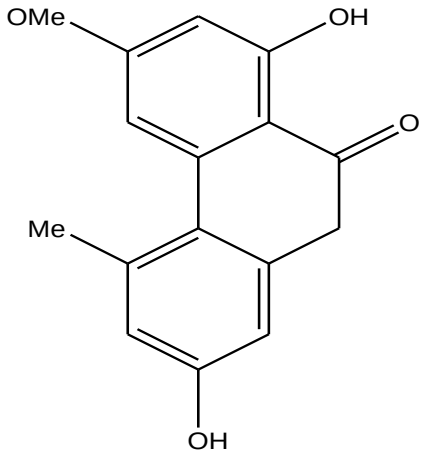


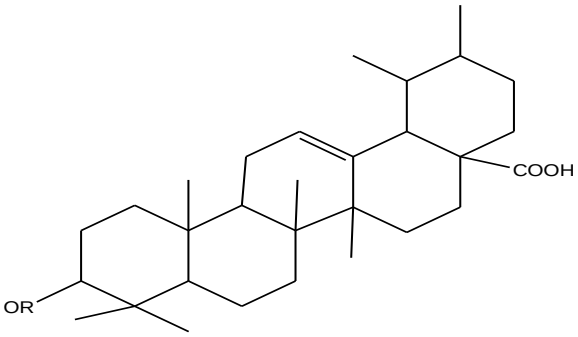
Figure 4: Variation of Corrosion Penetration Rate of *A. djalonensis* Extract with Time.



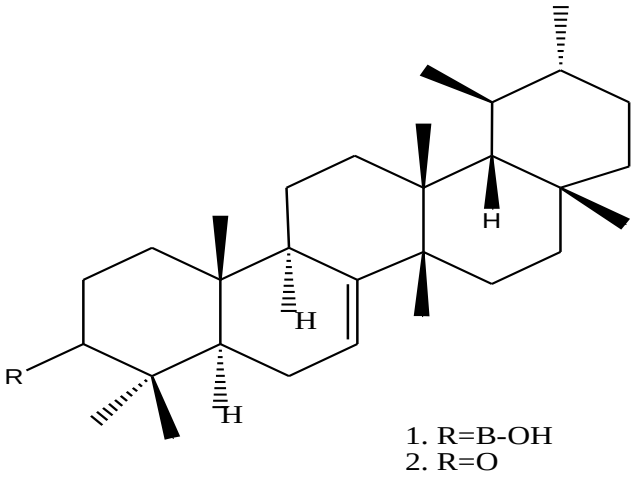
Structure I: Dibenzo-α-pyrone.



Structure II: Djalonensone.



Structure III: Ursolic Acid.



Structure IV: 1=Baurenol; 2=Baurenone.

This situation leads to protection of metal surface from the attack of the aggressive acid solution. The degree of protection increases with increase

in the surface fraction occupied by the adsorbed molecules. Sethuraman and Raja [9] also reported that adsorption of extract of *Datura metel* as an inhibitor for mild steel in acidic medium, was through adsorption of the phyto-constituents on mild steel.

Adsorption Behavior and Thermodynamics

Since corrosion inhibition is related to the adsorption of the inhibitor molecules on the metal surface, The surface coverage θ of the adsorption process was calculated using the equation:

$$\theta = \frac{IE}{100} \quad \textbf{(5)}$$

Thus a plot of C/θ and C should be a straight line. Indeed, a straight line was obtained and is as shown in Figure 5 with almost unity slope.

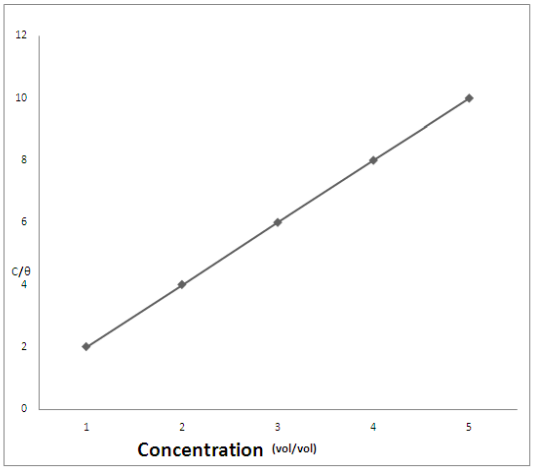


Figure 5: Plots of C/θ with Concentration (C).

This is indicative the adsorption follows Langmuir adsorption isotherm. Langmuir adsorption isotherm could be represented as:

$$\frac{C}{\theta} = \frac{1}{k} + C \quad \textbf{(6)}$$

Where k is the adsorption constant and,

$$\ln k = \ln \frac{1}{55.5} - \frac{\Delta G_{ads}}{RT} \quad \textbf{(7)}$$

The standard free energies of adsorption were calculated using Equation 7 where one molecule of water is replaced by one molecule of inhibitor. The numerical value of $(\frac{1}{55.5})$ in Equation 7 stands for the molarity of water.

The value of ΔG^{o}_{ads} adsorption of extract components was found to be – 35.34 kJ mol-1 which was in good agreement with what was obtained by other workers [2 and 10].The negative value of ΔG^{o}_{ads} indicated the adsorption of the plant extract on the metal surface is a spontaneous process.

Effect of Temperature

The effect of temperature on the corrosion of aluminum was studied on inhibited and uninhibited solutions in the temperature range of 30℃-50℃, and %IE was plotted as a function of concentration of WEAD and is shown in Figure 6. It is evident that inhibition increases with concentration of the plant extract and decreases with increasing temperature. It is presumed that increase in temperature reduces inhibitor adsorption and promotes metal dissolution.

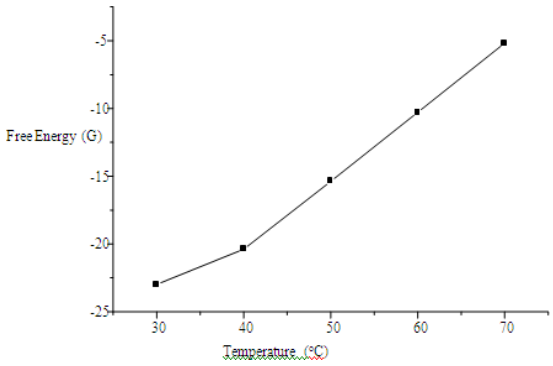


Figure 6: Plots of Free Energy of Adsorption against Temperature.

The activation energy of corrosion process in the absence and presence of plant extract could be calculated with the help of the transition state equation:

$$k = A \exp(-E_a^*/RT) \quad \textbf{(8)}$$

Where Ea is the energy of activation, A is the frequency factor, R is the universal gas constant, T is the absolute temperature and k is the rate of corrosion reaction which is directly proportional to the corrosion rate. Thus a plot of log k against 1/

T should be a straight line, where, Ea can be readily computed from the slope of the straight line portion of the curves. The values of activation energy obtained from such plot (not shown) are given in Table 6.

Table 6: Activation Energy of the Corrosion Processes.

Concentration	Activation energy (kJ/mol)
0.5M H_2SO_4	28.62
10/10 (v/v)	26.95
20/20 (v/v)	24.25
30/30(v/v)	23.86.
40/40(v/v)	22.67
50/50(v/v)	21.85

It is evident from Table 6 that WEAD inhibits the corrosion reaction by increasing its activation energy. This is only possible through adsorption of WEAD on the metal surface probably through the formation of a complex of the type $(M—Inh.)_{ads}$ complex on the metal surface. This adsorbed complex may be chemisorptions judging from the high value of energy of activation.

This type of inhibitor belongs to the third category of inhibitors [15] which are good inhibitors at ordinary temperature but exhibit considerable loss of inhibitive properties at elevated temperature.

CONCLUSION

- AEAD acts as a good inhibitor for acid corrosion of aluminum.
- The inhibition action of the plant extract is due to the presence of various functional groups on the chemical compounds (I-IV) through synergetic action.
- The inhibition efficiency decreased with the increase in temperature.
- Inhibition is presumed to be via adsorption of the organic compounds on the aluminum surface.
- The adsorption follows Langmuir adsorption isotherm.

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