

Corrosion of Aluminum in Water-Ethanol Mixture in the Presence of *Anthocleista vogelii* Extract.

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ABSTRACT

The inhibitive action of leaf extracts of *Anthocleista vogelii* on aluminum corrosion in water-ethanol mixture was studied using gravimetric techniques. The results indicate that the leaf extract of *Anthocleista vogelii* functioned as a good inhibitor. The results of the study revealed that weight loss decreases with an increase in time spent in the water-ethanol extract of *Anthocleista vogelii*. Values of the inhibition efficiency obtained are dependent upon the concentration of the inhibitor. The Inhibition Efficiency of the extract was also found to vary with percentage of water present and the time of immersion at room temperature. The inhibition efficiency was found to increase as the time of immersion increases and decreases as the percentage water present increases. Physical adsorption mechanism has been proposed for the adsorption of the inhibitor.

(Keywords: *Anthocleista vogelii*, corrosion, inhibition efficiency, adsorption)

INTRODUCTION

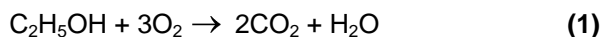
Aluminum and its alloys are very attractive materials for engineering applications due to their low cost, light weight, high thermal and electrical conductivity, and mechanical strength [1]. Aluminum and its alloys are found attacked by fuel methanol. A 2% H₂O in methanol and 5% H₂O and 15 mg ethanoic acid in ethanol have been found to cause severe corrosion of automotive parts [2].

Alcohols are of increasing interest as fuel substitutes for coal, oil, or natural gas [3]. The use of alcohol as fuel for internal combustion engines either alone or in combination with other fuels [4, 5, 6] has been given much attention, mostly because of its environmental and long term

advantages over fossil fuels. Alcohols can be derived from renewable energy resources such as biomass in conjunction with solar power. When alcohol is mixed into gasoline the result is gasohol [6]. Alcohol is also increasingly used as oxygenate for gasoline as replacement for methyl tertiary butyl ether (MTBE) [7].

Ethanol has hygroscopic qualities in it that attracts and mixes with water. At lower concentrations of water (up to 0.5% volume at 60°F), the alcohol will mix and remove the water as the fuel is burned and not harm the engine. At higher concentrations, the water will separate from the fuel and pool at the bottom of its container. This "phase" separation form of water in fuel can cause rust and possibly damage the engine. Fuel that is an E10 blend cannot absorb enough moisture out of the air to cause this phase separation [7].

Ethanol is flammable and pure ethanol burns more clearly than many other fuels. When fully combusted, its combustion products are CO₂ and H₂O, which are by-products of regular cellulose waste decomposition.



These days a large number of Brazilian vehicles run on ethanol rather than on conventional hydrocarbon fuels [5, 6]. Ethanol has a much higher octane rating (about 115) than ordinary gasoline [5, 8].

The aim of the present work is to investigate the inhibitive effect of extract of *Anthocleista vogelii* on aluminum in contaminated ethyl alcohol. The extracts of plants and other phytochemical materials have been tested as corrosion inhibitors for aluminum [9 – 14]. These extracts offer several advantages over traditional inhibitors because they have low toxicity, they are environmentally acceptable, readily available, and

renewable and above all they have potentially low cost.

MATERIALS AND METHODS

Aluminum sheets with nominal composition 96% Al, 0.8% Si, 0.7% Fe, 0.4% Cu, 1.2% Mg, 0.35% Cr, 0.25% Zn, and 0.15% Ti was procured from Tower Aluminum Plc, Lagos. The aluminum sheets were cut into 2 x 2 cm coupons. Before use, the specimens were abraded with different grades of silicon carbide paper up to 1200 grade, washed with distilled water, degreased with acetone, and dried with an air jet. The weight of the specimens before and after immersion time was determined using high precision Metler Balance model 2735. The corrosion products were cleansed with Clarke's solution. The weight loss (Tables 1 and 2) of the metal after experimental period is given by:

$$\Delta w = w_1 - w_2 \quad (2)$$

where w_1 and w_2 are the weights of the specimens before and after exposure to the corrosive solution in the absence and presence of

plant extract. The percentage inhibition efficiency (%IE) and the degree of surface coverage (θ) were calculated from the following equations:

$$\% IE = \frac{1 - \Delta w_{inh}}{\Delta w_{free}} \times 100 \quad (3)$$

$$\theta = \frac{IE}{100} \quad (4)$$

The values of inhibition efficiency and the degree of surface coverage (θ) calculated from Equations 3 and 4 are shown in Table 3.

The corrosion rate (R), for aluminum in alcohol and alcohol-water mixture for the immersion periods was determined in $\text{mg dm}^{-2} \text{day}^{-1}$ using equation:

$$R (\text{mdd}) = \frac{W}{AT} \quad (5)$$

where W is the weight loss (mg), A is the area of the specimen coupons (dm^2) and T is the exposure time (day). The corrosion rates are shown in Table 4.

Table 1: Weight Loss (mg) of Aluminum in Water-Ethanol Mixture in the Absence of Inhibitor at Room Temperature.

	2 HRS	4 HRS	6 HRS	8 HRS	10 HRS
0%	0.0032	0.0035	0.0039	0.0044	0.0049
2%	0.0036	0.0039	0.0045	0.0053	0.0057
4%	0.0041	0.0045	0.0051	0.0058	0.0062
6%	0.0047	0.0052	0.0059	0.0068	0.0076
8%	0.0054	0.0058	0.0067	0.0083	0.0093
10%	0.0063	0.0068	0.0075	0.0091	0.0102

Table 2: Weight Loss of Aluminum in Water-Ethanol Mixture in the Presence of Inhibitor at Room Temperature.

	2 HRS	4 HRS	6 HRS	8 HRS	10 HRS
0%	0.0018	0.0015	0.0011	0.0008	0.0006
2%	0.0021	0.0017	0.0014	0.0011	0.0009
4%	0.0026	0.0021	0.0018	0.0014	0.0011
6%	0.0032	0.0029	0.0025	0.0023	0.0020
8%	0.0039	0.0035	0.0031	0.0025	0.0020
10%	0.0048	0.0043	0.0036	0.0031	0.0028

Table 3: Inhibition Efficiency of Aluminum in Water-Ethanol Mixture in the Presence of Inhibitor at Room Temperature.

	2 HRS		4 HRS		6 HRS		8 HRS		10 HRS	
	I%	θ	I%	θ	I%	θ	I%	θ	I%	θ
0%	43.75%	0.438	57.14%	0.571	71.79%	0.718	81.82%		87.76%	0.878
2%	41.67%	0.417	56.41%	0.564	68.89%	0.689	79.25%		84.21%	0.842
4%	36.59%	0.366	53.33%	0.533	64.71%	0.647	75.86%		82.26%	0.823
6%	31.91%	0.319	44.23%	0.442	57.63%	0.576	66.18%		73.68%	0.737
8%	27.78%	0.268	39.66%	0.397	53.73%	0.537	69.88%		78.49%	0.785
10%	23.81%	0.238	36.76%	0.368	52.00%	0.520	65.93%		72.55%	0.726

Table 4: Corrosion Rate (mmpy) of Aluminum in Water-Ethanol Mixture in the Presence of Inhibitor at Room Temperature.

	2 HRS	4 HRS	6 HRS	8 HRS	10 HRS
0%	0.0098	0.0041	0.0020	0.0011	0.00066
2%	0.0115	0.0046	0.0025	0.0015	0.00098
4%	0.0142	0.0057	0.0033	0.0019	0.0012
6%	0.0175	0.0079	0.0046	0.0031	0.0022
8%	0.0213	0.0096	0.0056	0.0034	0.0022
10%	0.0262	0.0118	0.0066	0.0042	0.0031

The alcohol water-mixtures of the following composition 2%, 4%, 6%, 8%, and 10% were prepared. The test pieces were immersed in 250 ml of test solution with and without plant extract.

plots of corrosion rate with time in the presence of plant extract. It was observed that corrosion rate decreases with immersion time. This trend is probably due to the fact that adsorption and surface coverage increases with concentration.

RESULTS AND DISCUSSION

Tables 1 and 2 show the mass losses in the absence and presence of plant extract while Figures 1 and 2 show the weight loss – time curves for the corrosion of aluminum in ethanol and water – ethanol mixture in the absence and presence of Anthocleista extract at 30°C. It is observed from the tables and figures that the weight loss decreased and therefore the corrosion inhibition strengthened with increase in plant extract concentration. The weight loss was also found to increase with percentage water concentration (Figure 3).

The near linearity of the plots (Figures 1 and 2) is presumed to be due to the absence of insoluble surface film characterized of aluminum during corrosion. Thus the surface is enveloped from the corrosive medium.

The percentage inhibition efficiency increases with additive time (Figure 4). Figure 5 shows the

Adsorption Isotherm

The surface coverage (θ) for different inhibitor concentration (C) is presented in Table 3. The degree of protection increases with increase of the surface fraction occupied by the adsorbed molecules. As the extract concentration is increased, the number of the adsorbed molecules on the metal surface increases; a phenomenon we referred to as population effect. In general, θ increases with increasing C. The correlation between C, θ and the energy of adsorption can be determined by plotting an adsorption isotherm and by calculation.

Figure 6 suggests that the experimental data fitted the Langmuir adsorption isotherm relationship. This isotherm postulates that there is no interaction between the adsorbed molecules and the energy of adsorption is independent on θ .

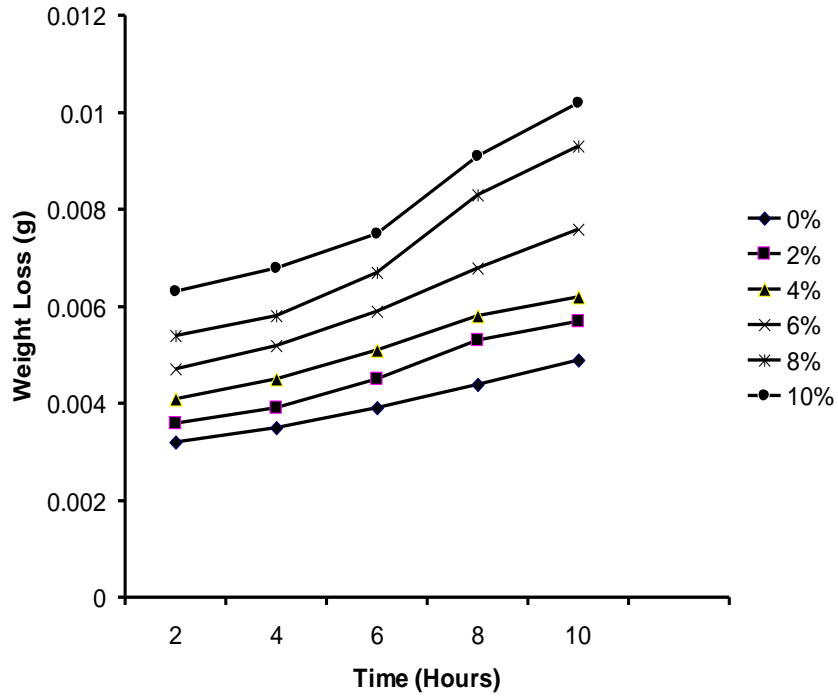


Figure 1: Variation of Weight Loss with Time in Water-Ethanol Mixture in the Absence of *Anthocleista vogelii* Leaf Extract.

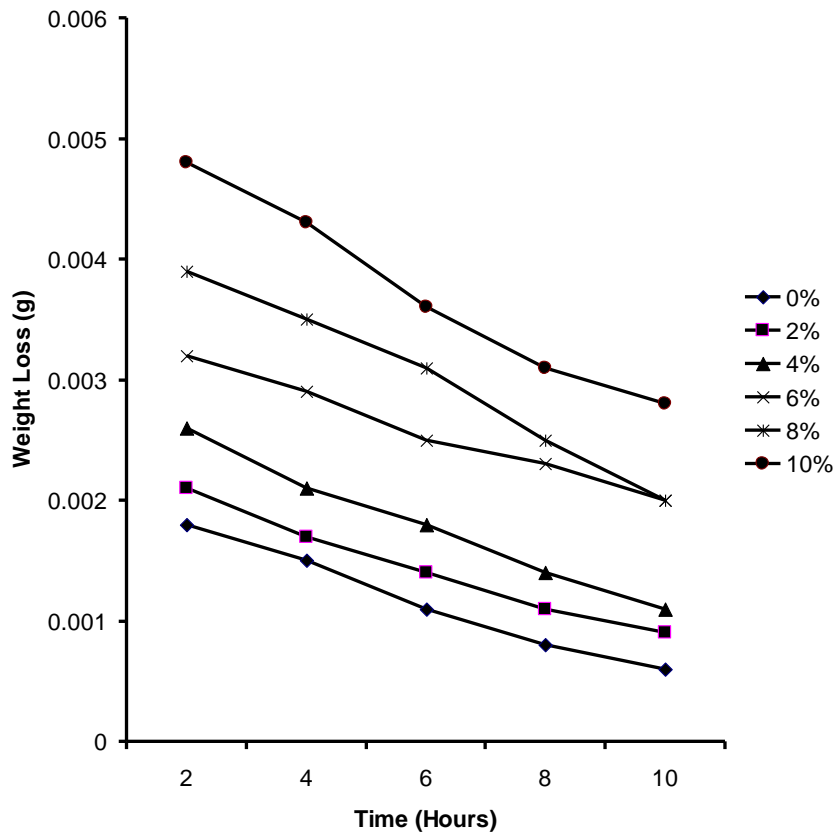


Figure 2: Variation of Weight Loss with Time in Water-Ethanol Mixture in the Presence of *A. vogelii* Leaf Extract.

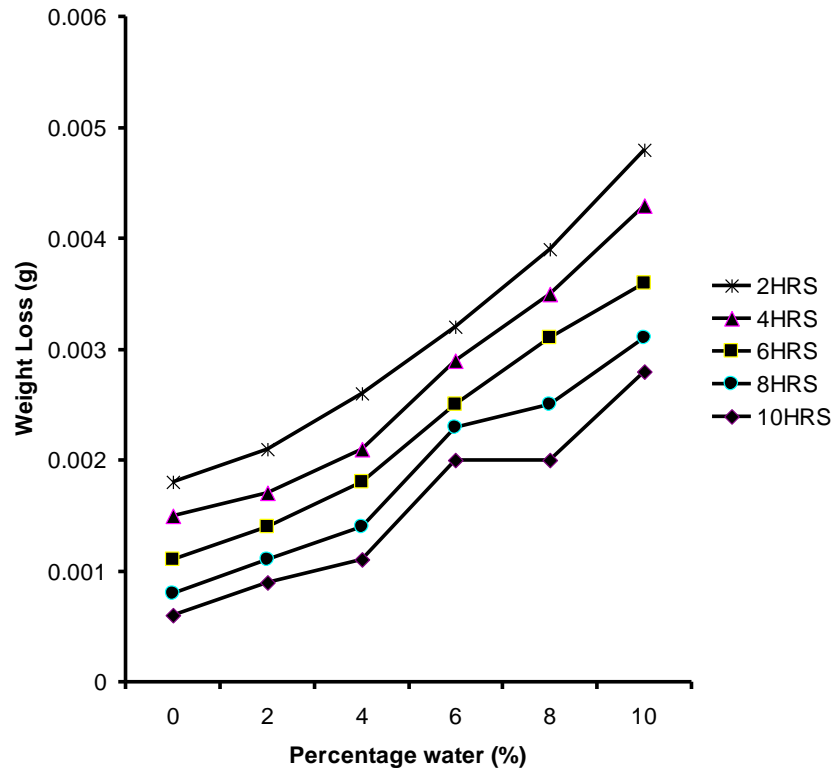


Figure 3: Variation of Weight Loss with Percentage of Water Concentration in the Presence of *A. vogelii*.

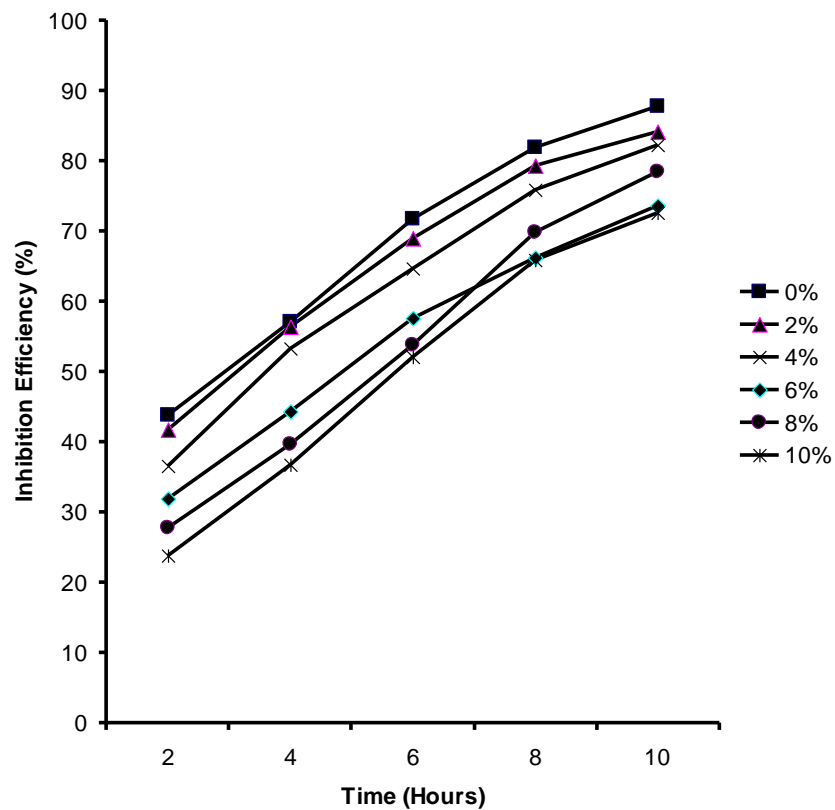


Figure 4: Variation of Inhibition Efficiency with Time in Water-Ethanol Mixture in the Presence of *A. vogelii* Leaf Extract.

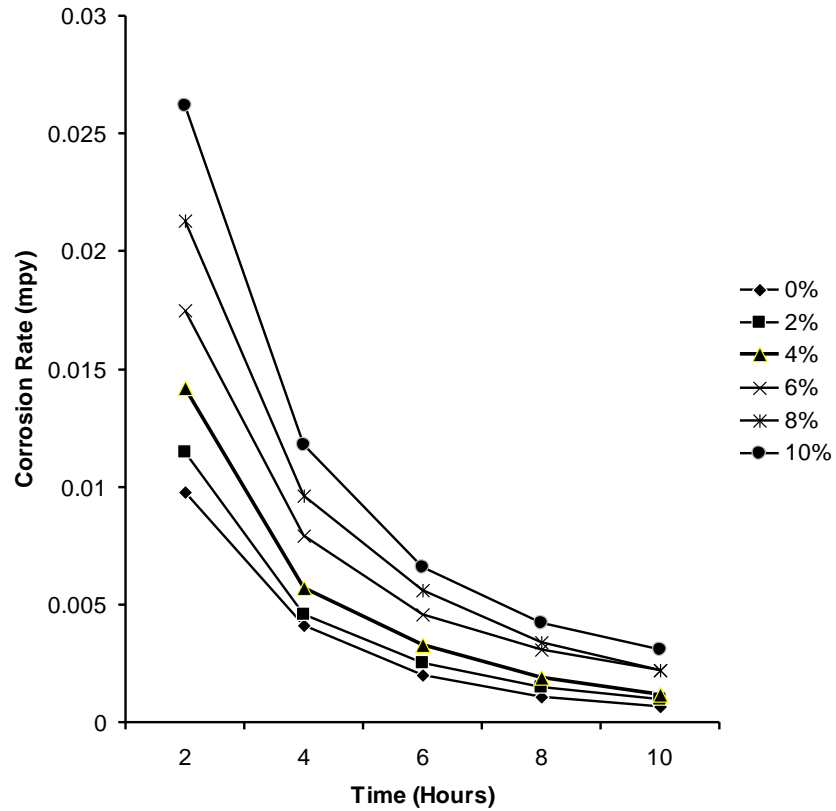


Figure 5: Variation of Corrosion Rate with Time in Water-Ethanol Mixture in the Presence of *A. vogelii* Leaf Extract.

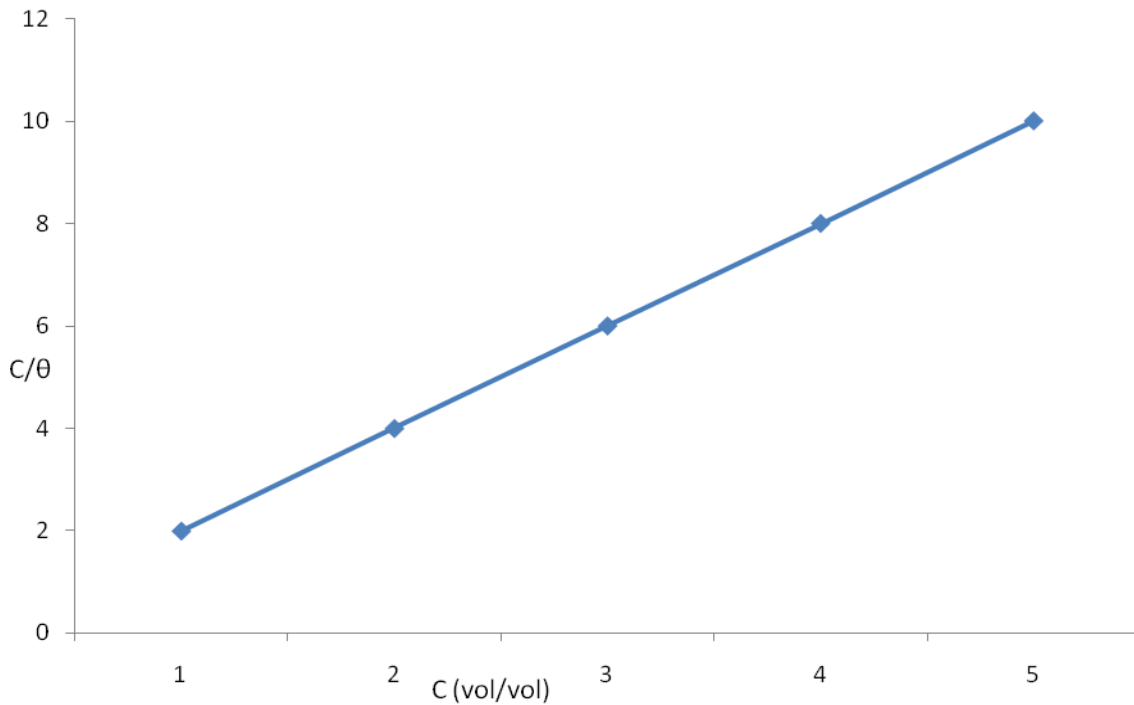


Figure 6: Langmuir Adsorption Isotherm.

Langmuir adsorption isotherm can be represented using the following equation:

$$\frac{C}{\theta} = \frac{1}{k} + C \quad (5)$$

where C is the extract concentration and k the equilibrium constant for adsorption, k is evaluated from the intercept of the plot and is related to the standard free energy of adsorption, ΔG_{ad}° by:

$$\ln k = \frac{1}{55.5} - \frac{\Delta G_{ad}^{\circ}}{RT} \quad (6)$$

where $(1/55.5)$ is the standard molar of water in the solution. From the plotted and calculated data, the values of k and ΔG_{ad}° are 58.76 and $-20.12 \text{ kJ mol}^{-1}$ for the plant extract.

These values are indicative of physical adsorption on the transfer of unit mole of plant extract from the solution onto the Al surface. The negative sign of the free energy of adsorption indicates that the adsorption of the inhibitor molecules at the Al surface is a spontaneous process.

Anthocleista vogelii

The tree is perennial, 5 – 18m high with smooth light grey bark, sparsely branched at the top with a spreading crown and spines in pairs on the branchlets. The bark and the root are used to treat dropsy, swelling, oedema, and gout, while the leaf bud is used as an antidote against stings and bites, etc. [17].

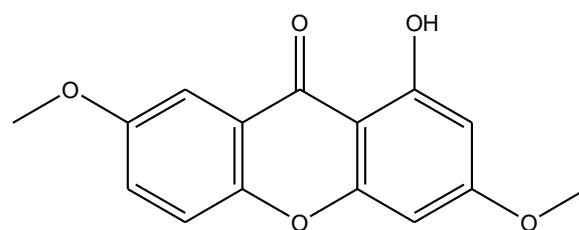
The presence of the following compounds has been reported (Figure 7):

1-hydroxy-3,7-dimethoxyxanthone;
1-hydroxy-3,7,8-trimethoxyxanthone [18]; and
1,8-dihydroxy-3,7-dimethoxyxanthone [19].

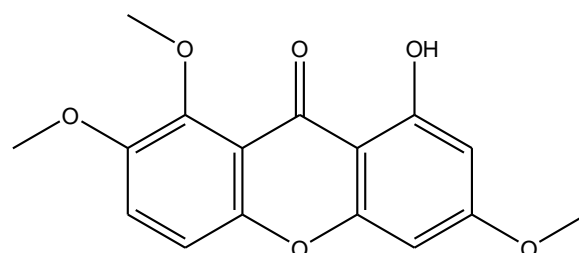
The *A. vogelii* extract therefore is a mixture of many organic compounds. However for the purpose of the present work the presence of 1-hydroxy-3,7-dimethoxyxanthone; 1-hydroxy-3,7,8-trimethoxyxanthone, 1,8-dihydroxy-3,7-dimethoxyxanthone are most pertinent.

Organic compounds with hetero atoms had been shown to exhibit corrosion inhibition [20]. Thus

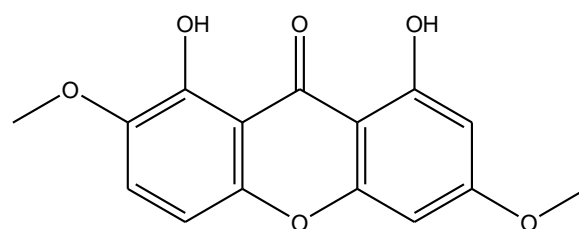
the presence of these compounds most of which contain hetero O-atoms and multiple bonds in their structures accords *Anthocleista vogelii* inhibitive properties in a synergetic manner. The adsorptions of these compounds on the metal surface make a barrier for mass and charge transfers. This situation leads to a protection of the metal surface from attack of the aggressive corrodant.



1-hydroxy-3,7-dimethoxyxanthone



1-hydroxy-3,7,8-trimethoxyxanthone



1,8-dihydroxy-3,7-dimethoxyxanthone

Figure 7: Compounds Reported in *Anthocleista vogelii* Extract.

If adsorption is the key to corrosion inhibition, then it is reasonable to suggest that these organic molecules are adsorbed on the metal surface through the various bondable oxygen atoms in their molecules. This inevitably leads to the formation of an adsorption complex of the type $(M-Inh)_{ads}$ complex on the metal surface. Consequently, the active sites on the metal

surface are blocked and metal dissolution is halted. This adsorbed complex could be physical or chemical.

CONCLUSION

Anthocleista vogelii was found to exhibit corrosion inhibition of aluminum in contaminated alcohol. The corrosion inhibition process was by the adsorption of the plant extract on the metal surface and follows Langmuir adsorption isotherm. The low value of the calculated standard free energy is suggestive of physical adsorption of the inhibitor molecules on the metal surface. While the negative value of ΔG° showed that the adsorption was a spontaneous process.

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