
Influence of Eco-Friendly Vernonia Amygdalina Leaf Extract on the Acid Corrosion of Aluminium

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Abstract: *The corrosion inhibition influence of Vernonia amygdalina extract on aluminium in 1M HCl solution was investigated using the gravimetric techniques at 30^oC and 60^oC temperatures. Aluminium coupons (type AA1060 and 98%) of dimension 3cm x 3cm were immersed into test solutions of uninhibited acid system and a five-test system containing different extract concentrations of 200mg/L, 400mg/L, 600mg/L, 800mg/L and 1000mg/L for 3 hours at 30^oC and 60^oC temperatures to check the effect of temperature increase in order to elucidate the nature of adsorption of the plant extract species onto the aluminium surface. Results obtained indicated that the Vernonia amygdalina was found to be a good green inhibitor of aluminium corrosion in a very aggressive, acidic, environment. The efficiency of inhibition increased with Vernonia amygdalina concentrations at 30^oC but decreased at 60^oC, which suggested physical adsorption mechanism, as the adsorption intermediate formed at the metal/solution interphase became soluble at higher temperature. Also, the inhibitor acted by being adsorbed on the surface of the aluminium according to classical Langmuir adsorption isotherm.*

Keywords: *Vernonia Amygdalina, Hydrochloric Acid, Aluminium, Adsorption, Inhibition Efficiency.*

1. INTRODUCTION

Corrosion is the degradation of the surface of a metal as a result of exposure of the metal surface to aggressive media such as acidic or alkaline medium. One of the major issues we face in the building / construction industries, including some technical installations, involving the use of alloy is corrosion, therefore, prevention procedure for the degradation of metal surfaces is of great importance in order to increase the lifespan of metals especially those usually exposed to some aggressive environments. Corrosion has become a necessary issue in industries where metals are predominantly used. In the automobiles industry, ships /



machinery, bridges, as a matter of fact, in most of the endeavour of man [18] The impact of corrosion encountered on daily basis, can both be direct and indirect. The direct effects involve a decrease of the usefulness of our possessions which are affected by corrosion. The indirect effects are experienced in the high cost of materials arising from the building in of corrosion prevention and corrosion control products, as well as maintenance. Furthermore, the major consequence of corrosion is the hazards and injuries to human which arises from some break down or structural failure (for example, cars, bridges, aircrafts) reduce the value of goods as a result of the reduction in the thickness of metal, thus, leading to a loss in the mechanical strength of the metal / structural failure [11]. In the quest to finding a lasting solution to the problem of corrosion, scientists and engineers have started to develop or discover substances that are capable of retarding the corrosion of metals. These substances are known as inhibitors. Inhibitors can be defined as substances or mixtures that can prevent, inhibit or minimize corrosion, in low concentration and in an aggressive environment, either acidic or alkaline. Corrosion inhibitors can be chemicals which could be man-made or natural and could be classified as organic or inorganic, based on their chemical nature; by their technical operation (mechanism) of action as cathodic or anodic or even a mix of anodic-cathodic, and by adsorption, or as oxidants or non-oxidants.

Corrosion protection using inhibitors has been employed in several areas which include; refinery units, cooling systems, boiler, oil and gas production units among others [1][3][6]. Most of these protective materials are man-made(synthetic) chemicals in nature [10][15] which is invariably high-priced and dangerous to the environment hence the need for a natural method of preventing corrosion becomes expedient and inevitable. Many plants found in nature have organic compounds such as tannins, alkaloid and amino acids, which have highly inhibitive properties and effect.[17][20] The principle of this corrosion inhibition is simply based on the adsorption of the molecules of the phytochemical present in the plant on the metal surface. This eventually replaces the molecules of water at the corroding sites or surfaces [5] [19].

In recent time, natural products or compounds such as plants, are used to inhibit corrosion, and to develop some new cleaning chemicals for a green environment. Plants, that are of pharmaceutical importance like the *Vernonia Amygdalina* have been selected because they are cheap (inexpensive) and as well as environmentally friendly. It is also readily available, and has become a renewable source for a very wide range of well sought-after inhibitors. Plant extracts are usually seen as a very rich source of naturally synthesized chemical compounds which can easily be extracted by some simple extraction procedures that are generally economical.

Also, considering the economic value of aluminium and its associated alloys, its protection against surface degradation or corrosion has indeed attracted great attention [22]. The corrosion inhibition property of aluminium arises from the ability of this metal (aluminium) to form a naturally stable oxide film, usually deposited on its surface in a very wide range of media. The oxide film formed readily undergoes degradation in different environments. The successful application of extrudate gum extract which are usually obtained from plants and used as corrosion inhibitors of aluminium in aggressive media like alkaline, has also been

reported [13]. Therefore, it is obvious that more findings on the use of natural products to fight corrosion are yet to be carried out since there are so many different plants that have these viable organic compounds with such inhibitive property and effect. Also, the need to study to the inhibition efficiency of some of these plant-based inhibitors like Vernonia Amygdalina at higher temperature becomes necessary. Therefore, this research aims at studying the corrosion inhibition efficiency of Vernonia Amygdalina at temperatures; 30°C and 60°C in order to ascertain the optimum temperature for maximum inhibition.

Vernonia amygdalina, also known as bitter leaf is a member of the pant family called daisy. It is a medicinal small shrub which grows in tropical Africa. Vernonia amygdalina grows, primarily, to a height of about 2–5 m. The leaves are elliptical and up to 20 cm long. Vernonia amygdalina leaf is known to have high crude protein, fat, crude fibre, ash and some minerals like Magnesium, Zinc, Iron etc, phytate and tannin. It is used for medicinal purpose to treat malaria fever, cough, bronchitis among other ailments owing to its antimalaria, antibacterial, and antifungal properties [21]



Fig. 1 Vernonia amygdalina leaf Source: [21]

Experimental

Material Preparation

Aluminium sheets used was of the type AA1060 and 98% purity [16] which contained alloying elements like silicon, manganese, zinc and magnesium, was obtained from the department of material and metallurgical engineering (workshop), Federal University of Technology Owerri and was mechanically pressed cut into coupons of dimension 3cm x 3cm. A 0.3 diameter hole was bored on each aluminium coupon [16] for effective suspension in the aggressive media. The coupons were first brushed with iron-brush to descale, then cleaned with absolute ethanol to degrease the surface of the aluminium coupons. The coupons were then dried in acetone and then stored in a moisture free desiccator before corrosion experiment test.

Preparation of Reagents and Inhibitor Extract

The reagents used were all of analytical grade, the corrosion medium employed was 1M HCl solution and was prepared from the stock solution using distilled water as the excess solvent. The leaf Vernonia amygdalina was obtained from a farm near the Nekede river, Nekede Owerri, Imo State. The leaves were washed with distilled water and dried for a week and



three days under the sun and then ground with a grounding machine to fine particles. The stock solution of the plant extract was prepared by refluxing 20g of the dried and ground *vernonia amygdalina* leaf in 1 dm³ capacity round bottom flask which contained 800ml of ethanol solution. The resulting green extract solution was cooled and filtered using a previously weighed filter [12]. Filtrate was stored while the residue was dried under the sun and reweighed, this was used to obtain the amount of plant materials extracted. From the stock solution of the extract. Different concentrations of 200mg/L, 400mg/L, 600mg/L, 800mg/L and 1000mg/L were made and the extract solutions were made up to 250ml in a round bottom flask with 1 M HCl which served as the corrodent.

Weight Loss Determination (Gravimetry Analysis)

The weight loss determination was employed on the 3 x 3 x 0.1cm previously brushed, cleaned (in absolute ethanol) and dried (in acetone) aluminium coupons as demonstrated by Eddy et al (2010). Two coupons labelled A and B were suspended in each of the 250ml test solutions containing different concentrations of 200mg/L, 400mg/L, 600mg/L, 800mg/L and 1000mg/L of the plant extract (inhibited system), using a polyester twine and glass hooks as well as in the blank (uninhibited) system which contained the corrodent (1 M HCl) for 3 hours at a temperature of 303K. After 3 hours, the corrosion products were removed by washing each coupon (retrieved from the test solution) in deionized water, and then rinsed in acetone and air-dried before re-weighing. The experiment was repeated at temperature of 333K so as to ascertain the effect of temperature increase, nature of adsorption of the plant extract species onto the surface of the aluminium coupons, determine the activation energy at each concentration and temperature (30°C and 60°C), as well as the heat of adsorption. In each case, the average weight loss was calculated and tabulated. The degree of surface coverage (θ), inhibition efficiency (%I) of the inhibitor, and the corrosion rate of aluminium (CR) were calculated using the equations 1,2 and 3 respectively [7]

Degree of surface coverage

$$(\theta) = 1 - (CR_{inh} / CR_{bl}) \dots\dots\dots 1$$

Where; CR_{inh} = corrosion rate of inhibited system

CR_{bl} = corrosion rate of uninhibited (blank) system

Inhibition Efficiency

$$(\%I) = 1 - (CR_{inh} / CR_{bl}) \times 100 \dots\dots\dots 2$$

Inhibition Efficiency (%I) = $\theta \times 100$

Where %I = inhibition efficiency.

Θ = degree of surface coverage.

$$\text{Corrosion rate (CR)} = \frac{\Delta W(\text{mg})}{AT(\text{cm}^2.\text{h})} \dots\dots\dots 3$$

Where; ΔW = average weight loss of the two coupons (mg)

T = Time of exposure (h)
 A = Total surface area of the coupon (cm²)

1. RESULTS AND DISCUSSION

Effect of concentration of Vernonia Amygdalina

The change in weight loss with time for aluminium coupon in the 1 M HCl solution by Vernonia amygdalina is shown in Table 1. This result shows that aluminium actually corrodes in 1 M HCl solution. The presence of the inhibitor (vernonia amygdalina) did decrease the extent to which the metal (aluminium) corroded. This clearly shows that the Vernonia amygdalina extract used for this study inhibited the corrosion of aluminium, therefore, can serve as an inhibitor in the corrosion of aluminium. It was generally observed that the weight loss decreased with an increase in the concentration of the ethanolic extract, which correlated with an anticipated increase in the kinetic of adsorption of the constituents of the vernonia amygdalina extract on the surface of the aluminium metal. The variation of the weight loss with percentage Inhibition Efficiency (% I.E.) at varying concentrations of the V. amygdalina extract is also shown in Table 1. The efficiency of inhibition was observed to increase with an increase in the concentration of the ethanolic extract of Vernonia amygdalina, at temperature 30°C. This can be attributed to the adsorption of molecules of inhibitor on the surface of the aluminium coupon. This observation corresponded with the result obtained and reported by Abiola & James (2010),[2] for zinc metal as well as aluminium in acidic media. The inhibition of aluminium corrosion by ethanolic extract of Vernonia amygdalina can be attributed to the binding mechanism of the extract unto the cathodic sites on the surface of the metal and its corrosion inhibition action, thus, increases with concentration. At 60°C, however, the inhibition efficiency of the extract as shown in Table 2, decreased with increasing concentration of the extract as compared with the values obtained at 30°C. This simply suggests that the adsorption mechanism of Vernonia amygdalina on the aluminium surface was physical.

Table 1. Average weight loss, corrosion rate, degree of surface coverage and Inhibition efficiency of the ethanolic extract of Vernonia amygdalina at 30°C

System	Coupon	Initial weight (g)	Final weight (g)	Average weight loss (mg)	Rate of Corrosion (mg/dm ³ /day)	Degree of surface coverage (θ)	Inhibition Efficiency (%)
200mg/L	A	2.3935	2.3631	31.5	1319.3717	0.9606	96.1
	B	2.3952	2.3626				
400mg/L	A	2.3678	2.3451	18.9	791.6230	0.9764	97.6
	B	2.3288	2.3138				
600mg/L	A	2.3809	2.3675	13.6	569.6335	0.9830	98.3
	B	2.2822	2.2685				
800mg/L	A	2.4120	2.4016	10.5	439.7906	0.9869	98.7



	B	2.3210	2.3104				
1000mg/L	A	2.3205	2.3134	7.1	297.3822	0.9911	99.1
	B	2.2678	2.2607				
Blank	A	2.3225	1.5738	799.2	33474.3456	-	-

Effect of temperature

The effect of temperature change on the corrosion inhibition of aluminium metal by ethanolic extract of Vernonia amygdalina was investigated using the logarithm form of Arrhenius equation, expressed mathematically as follows; [4] and [9].

$$\log (CR_2/CR_1) = E_a/2.303R (1/T_1 - 1/T_2) \dots\dots\dots 4$$

where CR₁ and CR₂ are the corrosion rates of aluminium at the temperatures T₁ (303 K) and T₂ (333 K), respectively. E_a is the activation energy and R is the gas constant. Values of Activation Energies (E_a) calculated from Equation (4) are presented in Table 3. From the results obtained, the activation energy increased with increase in the concentration of the inhibitor. These were within the range of values expected for a physical adsorption mechanism. Also, the corrosion activation energy increased from 19.3891 KJmol⁻¹ in the uninhibited system to 99.2740 KJmol⁻¹ in the inhibited system. The difference in the activation energy may indicate that Vernonia amygdalina affected the corrosion rate by decreasing the available sites for dissolution reaction. This observation is in agreement with the earlier suggestion of Vernonia amygdalina physisorption on the aluminium surface and the physisorbed molecules of the Vernonia amygdalina retarded aluminium dissolution by blocking cathodic areas and reduce the inherent reactivity of the metal at the adsorption sites [14] the inhibition efficiency of Vernonia amygdalina decreased with rise in temperature which suggested physical adsorption mechanism, so, it follows that the adsorption of ethanolic extract of Vernonia amygdalina on the aluminium surface was consistent with the mechanism of physical adsorption.

Table 2. Average weight loss, corrosion rate, degree of surface coverage and Inhibition efficiency of the ethanolic extract of Vernonia amygdalina at 60°C

System	Coupon	Initial weight (g)	Final weight (g)	Average weight loss (mg)	Rate of Corrosion (mg/dm ³ /day)	Degree of surface coverage (θ)	Inhibition Efficiency (%)
200mg/L	A	2.1675	1.3015	876.9	36728.7958	0.4514	45.1
	B	2.6761	1.7884				
400mg/L	A	2.3071	1.7521	561.0	23497.3822	0.6490	64.9
	B	2.6061	2.0391				
600mg/L	A	2.2334	1.7934	440.0	18429.3194	0.7247	72.5
	B	3.2980	1.8580				
800mg/L	A	3.2210	2.8689	352.3	14756.0209	0.7796	78.0



	B	3.1101	2.7577				
1000mg/L	A	3.2521	2.9611	247.0	10345.5497	0.8455	84.6
	B	3.2521	3.0091				
Blank	A	3.2210	1.6226	1598.5	66952.8795	-	-
	B	3.0120	1.4231				

Thermodynamic and adsorption considerations

The heat of adsorption (Q_{ads}) of ethanol extract of Vernonia amygdalina on the surface of aluminium was calculated using the mathematical expression below (Equation 5) [8]

$$Q_{ads} = 2.303R [\log (\theta_2 / (1 - \theta_2)) - \log (\theta_1 / (1 - \theta_1))] \times (T_1 T_2 / T_2 - T_1) \text{ KJmol}^{-1} \dots\dots\dots 5$$

where Q_{ads} is the heat of adsorption of Vernonia amygdalina, R is the gas constant, θ_1 and θ_2 are the degrees of surface coverage of the inhibitor at 303 K (T_1) and 333 K (T_2), respectively. Calculated values of Q_{ads} are also presented in Table 3. These values obtained are negative and progressively increase in value with increase in the concentration of the ethanol extract of Vernonia amygdalina. This shows that the adsorption of ethanolic extract of Vernonia amygdalina on the surface aluminium is exothermic and spontaneous, and consequently suggests a physical adsorption mechanism. The Langmuir and Flory Huggins adsorption isotherms were also used to study the adsorption behaviour of the ethanolic extract of Vernonia amygdalina on aluminium surface. The graph of C/θ against the concentrations for the Langmuir isotherm, on Fig 2, showed a straight-line graph with the slope approximately unity (one) which signified that the mechanism of adsorption of Vernonia amygdalina was through physical adsorption. Also, the graph of $\log(\theta/C)$ against $\log (1-\theta)$ from the equation; $\log(\theta/C) = \log K + x \log (1-\theta)$, for the Flory Huggins isotherm, on Figs 3 and 4, showed that the number of adsorbed molecules of the inhibitor on the aluminium surface was higher at 303K than that at 333K. This showed that the inhibition efficiency actually decreased as the temperature increased, and consequently suggested a physical adsorption mechanism.

Table3. Thermodynamic parameters for the adsorption of ethanolic extract of Vernonia amygdalina on the surface of aluminium

System	Temperature	Degree of surface coverage (θ)	Inhibition Efficiency (%)	Rate of Corrosion (mg/dm ³ /day)	Free energy of adsorption (KJ/g)	Heat of adsorption (KJmol ⁻¹)	Activation Energy (KJmol ⁻¹)
200mg/L	30°C	0.9606	96.1	1319.3717	-18.1667	-94.7765	93.0398
	60°C	0.4514	45.1	36728.7958	-10.5816		
400mg/L	30°C	0.9764	97.6	791.6230	-19.4992	-86.9225	94.8341

	60°C	0.6490	64.9	23497.3822	-12.8236		
600mg/L	30°C	0.9830	98.3	569.6335	-20.3427	-86.4056	97.2436
	60°C	0.7247	72.5	18429.3194	-13.8018		
800mg/L	30°C	0.9869	98.7	439.7906	-21.0092	-85.5420	98.2618
	60°C	0.7796	78.0	14756.0209	-14.6199		
1000mg/L	30°C	0.9911	99.1	297.3822	-21.9939	-84.2670	99.2740
	60°C	0.8455	84.6	10345.5497	-15.8283		
Blank	30°C	-	-	33474.3456	-	-	19.3891
	60°C	-	-	66952.8795	-		

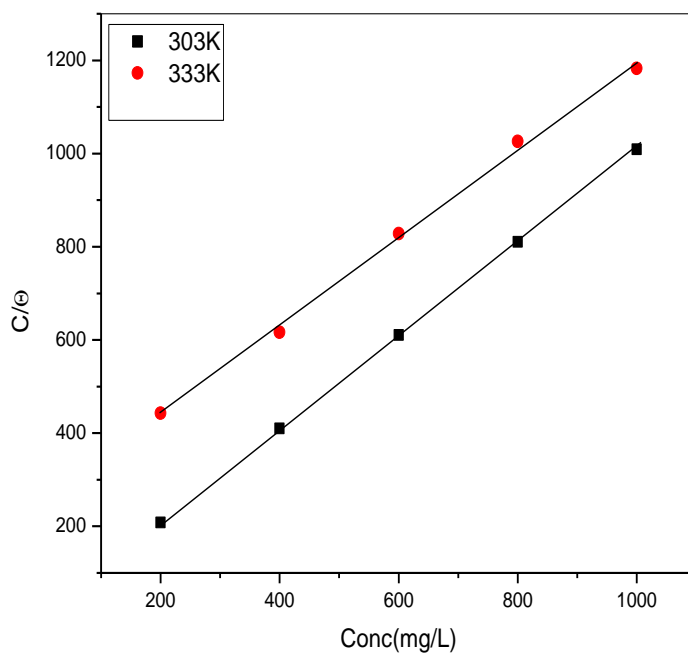


Fig 2. Langmuir isotherm for the adsorption of ethanolic extract of Vernonia amygdalina on the surface of aluminium at 303K and 333K

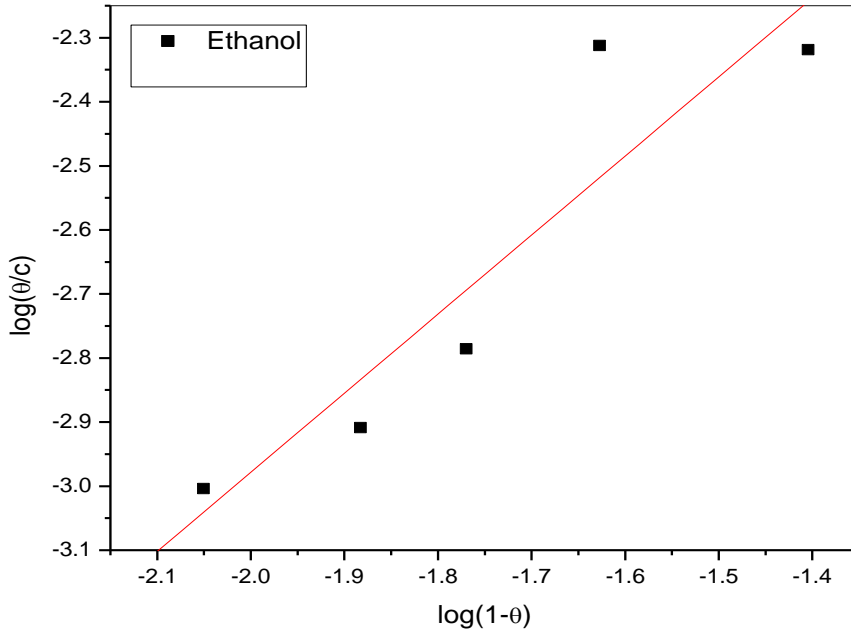


Fig 3. Flory Huggins isotherm for the adsorption of ethanolic extract of Vernonia amygdalina on the surface of aluminium at 303K

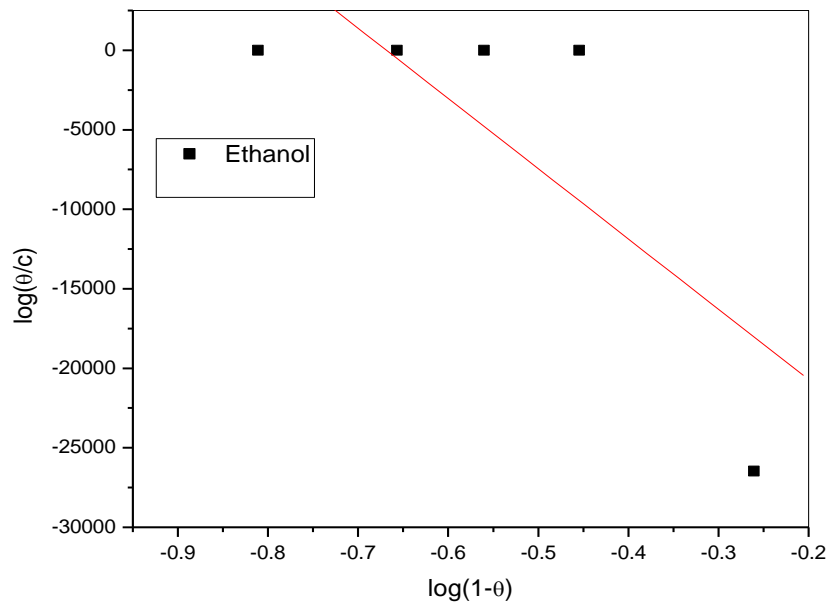


Fig 4. Flory Huggins isotherm for the adsorption of ethanolic extract of Vernonia amygdalina on the surface of aluminium at 333K



2. CONCLUSION

From the study, the following can be deduced;

The ethanolic extract of *Vernonia amygdalina* is an excellent eco-friendly adsorption inhibitor for the corrosion of aluminium metal in 1 M HCl solutions.

The percentage inhibition efficiency (% I.E.) of *Vernonia amygdalina* increased with concentration.

The adsorption process of the inhibitor was spontaneous, as well supported the mechanism of physical adsorption.

An optimum inhibition efficiency can be obtained or measured from ethanolic extract of *Vernonia amygdalina* by taking advantage of the period of contact of inhibitor, concentration of the inhibitor, and temperature.

The inhibitive effect of *Vernonia amygdalina* was by physical adsorption on the surface of the aluminium according to classical Langmuir adsorption isotherm.

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