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Research Paper

Acanthus montanus Extract as Sustainable and Eco-Friendly Corrosion Inhibitor of Mild Steel in Acidic Medium

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Abstract: *Acanthus montanus* (leaves, stem and root) extracts were studied as a sustainable and eco-friendly corrosion inhibitor in 1M HCl, using gravimetric technique. The plant extracts reduced corrosion rate of mild steel in the corrosive medium, thereby exhibiting corrosion inhibition property. The corrosion inhibition effect is attributed to the extract molecules being able to get absorbed to the metal surface creating a barrier between the acid and the mild steel. The adsorption of the extract molecules were fitted into Langmuir adsorption isotherm. Inhibition efficiency of the plant extracts increased with increase in concentrations of extracts but decreases with rise in temperature suggesting physisorption mechanism. The trend in values of apparent activation energy, coupled with the trend in values of heat of adsorption all supported the physisorption mechanism.

Keywords: *Acanthus montanus*, corrosion inhibition, adsorption, eco-friendly and organic inhibitor.

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Introduction

Corrosion is a natural process and it occurs as a result of the inherent tendency of metals to revert to their more stable compounds usually oxide. Most metals are found in nature in form of various chemical compounds called ores, and in the refining process energy is added to the ore to produce the metal in the pure state. It is this same energy that produces the driving force causing the metal to revert back to the more stable compound state, by corrosion process. Industries have invested so much in, preventing this scourge, because they depend immensely on metal and alloys which are prone to corrosion for industrial operations. In addition to this form of degradation, corrosion causes plant shutdown, waste of valuable resources, contamination of products, reduction in efficiency, costly maintenance and expensive over design^[1] As reported in^[2] preventive measures have been adopted over the years such as protective coating, cathodic protection, material selection, special design, feature and inhibition, but corrosion problems still occur which may be due to improper application of the measures or sufficient data or information on the cause of corrosion. Extensive work on corrosion control by inhibition, has covered areas

such as microbial inhibition, chemical inhibition, petrochemical inhibition and other synthetic or artificial forms of inhibition although these micro acids of inhibition measures are effective, for example lead compounds present in paint formulations are well known for their toxic carcinogenic effect, other corrosion inhibitors such as benzene nitrates and phosphorus, exhibit toxic and adverse environmental effect. However, the need to develop effective non toxic environmentally friendly features is the common jingle in science today^[4,5]. In this regard, many researchers have embarked on the use of organic inhibitor of plant sources to prevent corrosion of metals, of which their research results proved effective, and efficient. The expanded interest on organic inhibitors of plant source otherwise called green inhibitors is attributed to the fact that they are cheap, ecologically friendly and poses no environmental threat, and the fact that they are readily available, renewable source of materials and sustainable^[6]. The corrosion inhibition properties in many plant extracts is due their heterocyclic constituents like alkaloids, flavonoids, tannins etc. Again, it is suggested that medicinal plants poses good corrosion inhibition properties, since they are constituted of compounds

containing heteroatom's like N, S, O and P which are reported to have corrosion inhibiting properties^[6,7,17-21]. The above reasons lead to our interest in *Acanthus montanus*.

Acanthus montanus belongs to *Acanthaceae* family with common English name mountain thistle. It is a perennial herb growing to height of 1.5 meters. The leaves are shallow deeply lobed, toothed with short spines, dark glossy green above and pale green below. Flowers are pink to reddish in long event spikes. It is widespread throughout Africa, Romania, Greece, and Eastern Mediteran. *Acanthus montanus* is widely used in ethno medicine. It is used in Africa for treatment of urogenital infections, and urethral pain. In Cameroon it is used for pain inflammation and threatened abortion. The leaves infusion is used for cough and chest pains. Several compounds like β -sitosterol-3-O- β -D glucoside, palmitric acid, linaroside, homoplantagenin, 5,7,3-trihydroxy-6,4-dimethoxyflavone-7-O-glucoside, shikimic acid, Protochatevic acid, blepharin, and acetoside were isolated from *Acanthus montanus*^[22]. Since all these isolated compounds from *Acanthus montanus* contain functionalities with heteroatom (oxygen), which is reported in ^[6,7,17-21] to exhibit corrosion inhibition property, we suggest adding to *Acanthus montanus*'s medicinal values, it will possess good corrosion inhibiting properties. However this study investigates the inhibitory potentials of *Acanthus montanus* leaves, stem and root extract each, on corrosion of mild steel in 1M HCl solution using gravimetric technique.

Material and Methods

Materials used for the study were mild steel sheet of weight composition (Wt %) Mn (0.6), P (0.36), C (0.15) and Si (0.03), the rest is Fe. The sheet was mechanically pressed cut to form different coupons, each of dimension 3 X 3 X 0.1cm. Each coupon was degreased by washing with ethanol dried in acetone and preserved in a desiccator prior to use. All reagents used for the study were analar grade double distilled water was used for their preparation ^[8].

Extraction of plant: samples of *Acanthus montanus* leaves, stem, and root were collected from the plant in Okwe-ukwu Oboro in Ikwuano local government area of Abia state, Nigeria. The samples were cut to pieces to increase the surface area for easy drying, after which they were dried in laboratory oven at 50°C in Chemistry Laboratory, college of Physical and Applied Sciences, Michael Okpara University of Agriculture Umudike, Abia State, Nigeria. The dried samples were pulverized to powdered form, and 10g of the powdered samples each were refluxed in 400ml of 1M HCl solution for 3hrs.

After the reflux, the resultant solutions were allowed to cool and filtered and the filtrate collected and stored as stock solutions. The test solutions of 200mg/l, 400mg/l, 600mg/l, 800mg/l and 1000mg/l of the *Acanthus montanus* leaves, stem and root extracts in 1M HCl were prepared using dilution formula.

Gravimetric analysis: Weight loss experiment were conducted under total immersion conditions in 250ml of test solutions and maintained at 30°C, and 50°C for 3hrs. The test coupons which were weighed before immersion were retrieved at the end of 3hrs, scrubbed with brittle brush under running water until clean. The clean test coupon were dried in acetone and reweighed. The weight loss was obtained from the difference between initial weight of coupons before immersion and final weight after immersion.

Corrosion rates of the mild steel coupon in the solutions were calculated using equation 1

$$CR = \frac{\Delta Wt}{AT} \dots\dots\dots (1)$$

Where CR represents corrosion rate, A is surface area of the test coupon and ΔWt is the change in weight of the coupon and T is the time in days. The degree of surface coverage and inhibition efficiency were calculated using equation 2 and 3 ^[19].

$$\theta = (1 - \frac{CR_{in}}{CR_{bl}}) \dots\dots\dots (2)$$

$$\% = (1 - \frac{CR_{in}}{CR_{bl}}) \times 100 \dots\dots\dots (3)$$

Where % is inhibition efficiency, θ is degree of surface coverage, while CR_{in} and CR_{bl} are corrosion rates in solution containing the inhibitor and 1M HCl solutions without the inhibitor respectively.

The gravimetric analysis of mild steel coupon in 1M HCl solution in the absence of inhibitor and in the solutions containing different concentrations of *Acanthus montanus* leaves, stem and root extracts differently are represented graphically in figures 1 and 2.

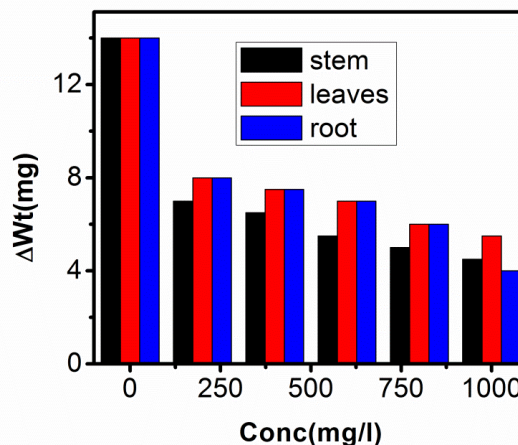


Figure 1: A graphical representation of weight loss against concentration of *Acanthus montanus* extract

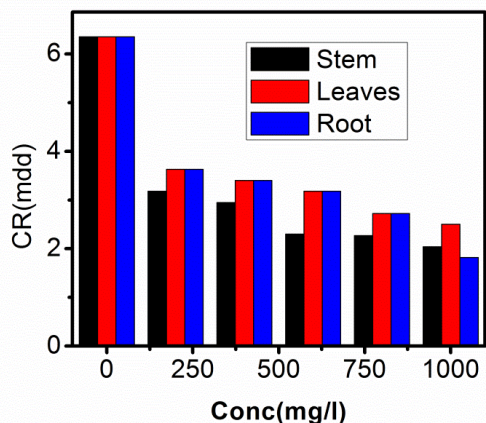


Figure 2: Graphical representation of corrosion rate against concentrations *Acanthus montanus* extracts

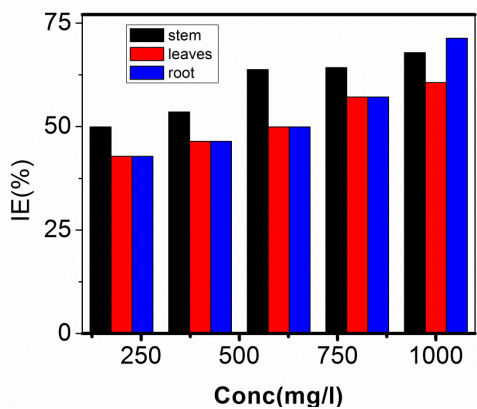


Figure 3: Graphical representation of inhibition efficiency against concentration *Acanthus montanus* extract

The graph in figure 1 shows plots of weight loss of the mild steel coupon in acid solution studied against various concentrations of *Acanthus montanus* leaves, stem and root extracts. The results show that weight loss reduced in solution containing the plant extracts when compared with blank solution. The reduction in weight loss became more pronounced with increase in extracts concentration.

The graph in figure 2, shows plot of corrosion rates against concentrations of *Acanthus montanus* leaves, stem and root extracts studied. The result of the graphs show a decreased in corrosion rates in the inhibited systems and It can be observed that corrosion rate continued to decrease as the concentration of the plant extracts increased. This reduction in corrosion rate in the inhibited system shows that the plant extracts were able to inhibit corrosion of mild steel in acid solution studied.

The inhibition efficiency and concentration variations can be seen in figure 3. Results from the graph show increase in

inhibition efficiency as concentration of *Acanthus montanus* leaves, stems, and root extract increases. From the figure 3 it can be observed that this effect was most susceptible in root extract followed by stem extract and then leave extract of *Acanthus montanus*. The inhibitory effect of the plant extract was as a result of the extract molecules been able to get absorbed to the metal surface there by creating a barrier between the corrodent and the metal surface.

Table 1: Presentation of free energy of (ΔG_{ad}^0) of root, stem, and leaves extracts of *Acanthus montanus*

System (mg/l)	ΔG_{ad}^0 (KJ). Leaves	ΔG_{ad}^0 (KJ). Root	ΔG_{ad}^0 (KJ). Stem
200	-3.96	-3.96	-3.24
400	-5.33	-5.33	-4.62
600	-6.01	-6.00	-4.57
800	-6.00	-5.99	-5.25
1000	-6.20	-4.99	-5.40

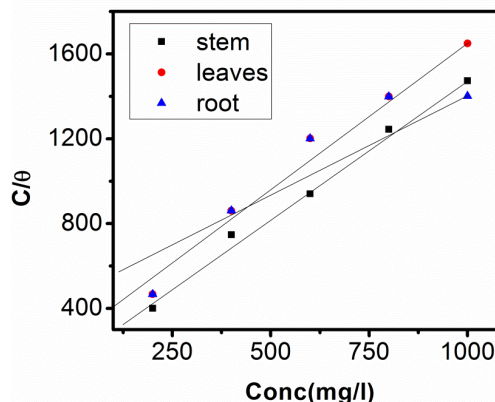


Figure 4: Langmuir isotherm

The relationship between the degree of surface coverage and *Acanthus montanus* leave, stem and root extracts can be represented by the Langmuir adsorption isotherm

$$\frac{\theta}{C} = C + \frac{1}{K_{ad}} \dots \dots \dots (4)$$

Where:

K is the constant for adsorption related to the free energy [ΔG_{ad}^0] by equation 5

$$K = \frac{1}{55.5} \exp\left(\frac{\Delta G_{ad}}{RT}\right) \dots \dots \dots (5)$$

Where ΔG_{ad}^0 is free energy of adsorption, R is is gas constant and T is temperature in Kelvin. Figure 4 shows a graph of C/θ versus concentration of leaves, stem and root extracts of that *Acanthus montanus* in 1M HCl solution to

be linear with intercept $\frac{1}{K}$ which suggest that the experiment fits into Langmuir adsorption isotherm the calculated values of ΔG_{ad}^0 are shown in table 1 the negative values indicates that plant extract spontaneously adsorbed to the mild steel surface in acid solution studied^[10,5].

Effects of Temperature

Temperature has a significant effect on metal corrosion rate and inhibition efficiency of the corrosion inhibitor when the corrosion reaction involves a cathodic process of hydrogen evolution, the corrosion rate increases exponentially with rise in temperature according to Arrhenius type dependence and inhibition efficiency decreases as temperature rises.^[5,7,8,11] Figure 5 illustrates the effect of change in temperature on inhibition efficiency of *Acanthus montanus* leaves, stems and root extracts on corrosion of mild steel in 1M HCl solution.

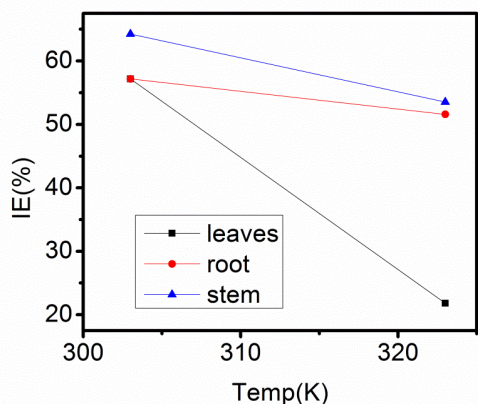


Figure: 5 A plot of inhibition efficiency against temperature

Inhibition efficiency in the concentration studied decreased as temperature increased. This observation can be explained with respect to the characteristics features of the cathodic process of hydrogen evolution, where decreased in the reaction with rise in temperature lead to an increase in the rate of cathodic reaction^[5,7,11,12]. This effect far overshadows the adsorption and inhibitive effect of *Acanthus montanus* because the enhanced rate of hydrogen gas evolution increasingly agitate the interface, which hinders inhibitors adsorption and also promote dispersal of adsorbed inhibitors^[10,13]. This marked reduction in inhibition efficiency with rise in temperature could be attributed to the shift of the adsorption desorption equilibrium towards desorption. This behavior suggests that *Acanthus montanus* leaves, stem and root extracts where physically adsorbed on the mild steel surface^[9,11].

The reaction between corrosion rate and temperature often expressed by Arrhenius equation:

$$K = A \exp\left(\frac{-Ea}{RT}\right) \dots \dots \dots (6)$$

Where *Ea* is the activation energy, *A* is the Arrhenius pre-exponential factor and *R* is the gas constant.

The reaction in equation 6 can be expressed as equation 7 to relate corrosion studies.

$$\log\left(\frac{CR_2}{CR_1}\right) = \frac{Ea}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \dots \dots \dots (7)$$

Where *CR₁* and *CR₂* are the corrosion rates at temperatures *T₁* and *T₂* respectively. Other parameters retained their previous meaning. The apparent activation energy (*Ea*) for mild steel coupons in absence and presence at *Acanthus montanus* where evaluated using equation 7 above. Activation energy is observed from table two to increase the inhibited system containing *Acanthus montanus* leaves, stem and root extracts respectively, such behavior coupled with a decrease in inhibition efficiency as temperature rises is evidence of physisorption interaction between the extract specie and mild steel surface^(14, 15, 16). Another thermodynamic parameter which further describes the adsorption mechanism operative in the corrosion inhibition process is the heat of adsorption (*Q_{ad}*) it is related to the surface coverage through the relation in equation 8.

$$Q_{ad} = 2.303R \left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right) \right] \times \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \dots \dots \dots (8)$$

Where *Q_{ad}* is heat of adsorption, θ_1 and θ_2 are degrees of surface coverage at temperatures *T₁* and *T₂* the calculated values of heat of adsorption shown also in table 2 are all negative. The negative values of heat of adsorption further supports that adsorption was spontaneous and physisorptive^[5, 7, 8, 11,13].

Table 2: Presentation activation energy (Ea) and heat of adsorption (Q_{ad})

System	Ea (KJ)	Q _{ad} (KJmol ⁻¹)
Blank	33.71	-
Leaves(800mg/l)	58.23	-2.65 x 10 ⁻⁶
Root (800mg/l)	38.71	-3.83 x 10 ⁻⁶
Stem (800mg/l)	49.26	-6.02 x 10 ⁻⁶

Conclusion

- Extract of *Acanthus montanus* leaves, stems, and roots separately, effectively inhibited corrosion of mild steel in 1mHCl solution.
- The inhibitive effect resulted from adsorption of *Acanthus montanus* stems, leaves and root extract molecules on mild steel surface, fitting into Langmuir adsorption isotherm.
- Inhibition efficiency generally increases with *Acanthus montanus* extract concentration but decreases with rise in temperature suggesting physisorption mechanism.
- The trend of values of activation energy, and heat of adsorption confirmed the adsorption mechanism to be physical.

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