Senna alata ACID EXTRACT AS ECO-FRIENDLY CORROSION INHIBITOR IN ACIDIC MEDIUM

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ABSTRACT

Senna alata leaves, root and stem extracts respectively were studied as corrosion inhibitor for mild steel in 1M HCl at temperatures 30^{o}C, 50^{o}C and 60^{o}C using gravimetric technique. The extracts were found to inhibit corrosion of mild steel in acidic medium. The inhibition efficiency increased with increase in concentration of the extracts, with the leaves and stem extracts showing maximum inhibition efficiency in 800mgl^{-1} of the extracts. The inhibition efficiency decreased with rise in temperature between the temperature of 30^{o}C and 50^{o}C but increased with rise in temperature between 50^{o}C to 60^{o}C suggesting a mixed adsorption mechanism of chemisorptions/physisorption of the plant extract on the mild steel surface. The trend in calculated values of apparent activation energies, free energy of adsorption and heat of adsorption provided evidence of adsorption and chemisorption mechanism was confirmed. Adsorption of extract molecules on mild steel surface was found to fit into Langmuir adsorption isotherm.

1.0 INTRODUCTION

Most metals used in construction of facilities are subjected to corrosion. This is due to the high energy content of the elements in metallic form. In nature, most metals are found in chemical combination with other elements. These metallic ores are refined by man to form metals and alloys. As the energy content of the metals and alloys is greater than that of their ores, chemical combination of the metals to form ore-like compounds becomes a natural process.

Corrosion of metals takes place through the action of electrochemical cells, although this single mechanism is responsible in corrosion, corrosion of metals can take many forms. Through an understanding of the electrochemical cell and how it can act to cause the various forms of corrosion, the natural tendency of metals to suffer corrosion can be overcome.

The rate of corrosion of metals can be controlled by reducing the aggressiveness of the medium, or by isolating the metals from the liquid. The latter can be done by coating the metal with a millimeter thick impervious non corroding material. These have wide spread use, but their effect may not be permanent because of brakes in the coating over time. Also in some systems coating might interfere with the process for which the equipment is used, they might change the heat transfer properties for example. To be on the safer side, corrosion inhibitors can be used. (1)

1.1 Corrosion inhibitor: Research results have proved the effectiveness of using inhibitors to retard corrosion. (1-12, 33-38). the inhibitors may be organic or inorganic compounds. Inorganic substances such as phosphates, chromates, dichromates and arsenates have been found to be effective inhibitors of metal corrosion, but a major disadvantage is their toxicity and as such their use has come under severe critisms. In alternative, organic corrosion inhibitors have been widely applied in solving corrosion problems because of their availability and ease of application. Organic corrosion inhibitors are usually composed of hetero-atoms such as N, S, and O in conjugate systems, with which they get absorbed to the metal surface (2 – 6). In contrary, some synthesized organic inhibitors could be hazardous to life which limits the choice of synthesized organic inhibitors as a solution. The current growing trend in bio-technology has geared many researchers towards discovering natural metal corrosion inhibitors of plants source which are in-expensive, readily available, renewable, environmentally friendly and ecologically acceptable.

It is stated in Abiola, (31) that the corrosion inhibition properties in many plants extracts is due to their heterocyclic constituents like alkaloids, tannins, flavonoids, phenols, saponins steroids etc. Again it is suggested that medicinal plants exhibit good corrosion inhibiting properties, because they are mostly constituted of compounds containing hectero-atoms like O, N, S, and P which are reported to have corrosion inhibiting properties. (5, 24-29). Owing to the medicinal value of *Senna alata* plant we suggest it will possess good corrosion inhibition properties.

1.2 Plant description and Usage: *Senna alata* is an ornamental shrub belonging to the family *leguminosae caesalpiniodea.* The plant can be found in Nigeria, Malaysia, Australia, Thailand, tropical America and many other parts of the word. It bears a yellowish flower which produces dry dehiscent fruit, with seed characteristic of a legume. The plant is of a great medicinal value, it is known for its antifungi property and is therefore used for treatment of several skin diseases. *Senna alata* is also credited for treatment of haemorrhaid, constipation, niguinal hernia, intestinal parasites, heart failure, abdominal pain, oedema and as well as purgative. (32). It is reported in Douye *et al* (30) that *senna alata* contains phytochemicals like tannins, steroids, phenol, and saponins. The fact that *senna alata* is constituted of these phytochemicals and its exhibition of medicinal properties lead to our reasoning that it will inhibit corrosion of metals. This study investigates the inhibitory effect of *senna alata* root, stem and leaves acid extract on corrosion of mild steel in 1M HCl solution using gravimetric technique.

2.0 MATERIALS AND METHODS

2.1 Materials preparation: Material used for the study were mild steel sheet of composition (wt%) Mn (0.6), P (0.36), C (0.15), and Si (0.03). The rest of the composition is Fe. The sheet was mechanically pressed cut to form different coupons, each of dimensions 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 the reagents used are of analytical grade and double distilled water was used for their preparation.

2.2 Preparation of Plant Extract: *Senna alata* leaves, root and stem were collected from plants around Michael Okpara University of Agriculture Umudike, Abia state, Nigeria. The samples were cut into small pieces to increase the surface area for easy drying. They were then dried in a laboratory oven at 50^{o}C and grinded to powdered form. 10g of the powdered *senna alata* root, stem and leaves separately were dissolved in 1M HCl and refluxed for 3hrs. The resultant solutions were filtered and the filtrate stored. The amount of dissolved samples in the extracts was calculated, and from the stock solution in mgl^{-1} the various test solution of the extracts in 200mgl^{-1}, 400mgl^{-1}, 600mgl^{-1}, 800mgl^{-1} and 1000mgl^{-1} studied were prepared. (39)

2.3 Gravimetric Analysis

Weight loss experiments were conducted under total immersion conditions in 250ml of test solution, maintained at 30^{o}C, 50^{o}C, and 60^{o}C for 3hrs. The test coupons which were weighed before immersion were retrieved at the end of 3hrs, scrubbed with bristle brush under running water until clean. The clean test coupons were dried in acetone and reweighed. The weight loss was taken as the difference between the weight of coupon before and after immersion (9 & 10). From the weight loss data corrosion rate was calculated using equation 1

$$CR = \frac{\Delta Wt}{AT} \quad \text{-- 1}$$

Where CR is the corrosion rate, A, is the surface area of the coupon, T, is time in days and ΔWt represents weight loss.

The inhibition efficiency in each concentration of senna alata leaves, stem and root extracts and the degree of surface coverage were calculated by comparing the corrosion rate in the absence and presence of the plant extract in the test solutions studied using the relationship in equation 2 as reported in Popova *et al* (11)

$$IE (\%) = \left(1 - \frac{CR_{in}}{CR_{bl}}\right) X\, 100 \quad \text{----------------------------- 2}$$

$$\theta = \left(1 - \frac{CR_{in}}{CR_{bl}}\right) \quad \text{…………………………….3}$$

Where IE is inhibition efficiency, CR_{in} is corrosion rate in inhibited system and CR_{bl} represent corrosion rate in absence of inhibitor

3.0 RESULT AND DISCUSSION

3.1 Gravimetric studies: The gravimetric analysis of mild steel coupon in 1M HCl solution in absence of inhibitor and in the solutions containing different concentrations of *Senna alata* leaves, stem and root extracts studied, are represented graphically in figure 1. The graphs show the corrosion rate of mild steel coupon in acidic solution studied against various concentrations of *Senna alata* leaves, root and stem extracts at 30^{o}C. The results show that corrosion rate reduced in the presence of the plant extract and this effect became more pronounced with increase in *Senna alata* leaves, Stem and root extracts. It is observed that the corrosion rate reduced more in leaves extracts concentration of 200mgl^{-1} than it did in root and stem extracts of that same concentration, but as the extract concentration increased to 800mgl^{-1} to 1000mgl^{-1} root extract reduced corrosion rate more that leave and stem extracts.

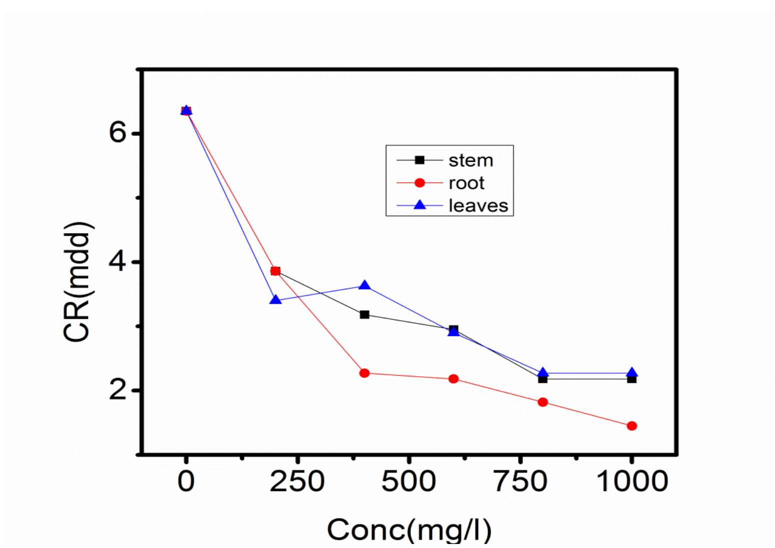

Figure1: **Corrosion Rate against Conc. of the Extracts**

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3.2 Corrosion Inhibition

The reduction in corrosion rate observed above indicates that the plant extracts has the ability to inhibit corrosion of mild steel in acidic medium. The extent of inhibition is shown figure 2

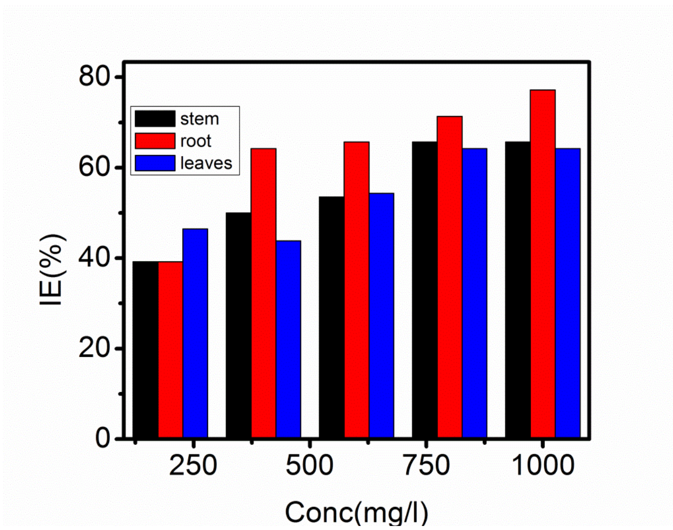

Figure 2: **Inhibition efficiency against Conc. of the Extracts.**

Figure 2 shows a plot of inhibition efficiency against concentration of leaves, stem and root extracts of *senna alata* in 1M HCl. Observations from the figure show increase in inhibition efficiency as the extract concentration is increased in leave, stem and root extracts. When the figure-2 is observed closely the results show that the leaves and stem extracts gave maximum inhibition efficiency at 800mgl^{-1} concentration, and when the concentration was increase to 1000mgl^{-1} no change in inhibition efficiency was observed. Unlike leaves and stem extracts, the root extracts, kept on increasing in inhibition efficiency as concentration increases, ranging, from 39.21% in 200mgl^{-1} to 77.17 in 1000mgl^{-1}. The corrosion inhibiting properties of the plant extract is suggested to result from the extract molecules ability to be adsorbed to the mild steel surface thereby creating a barrier between the metal and the corrodent.

3.3 Adsorption Consideration

Adsorption behavior of plant extracts can be studied using some adsorption isotherms, like Langmuir adsorption isotherm, or Temkins adsorption isotherms, or Fruedlich adsorption isotherm etc. Figure 3 below represents Langmuir adsorption isotherm of *Senna alata* leaves, root, and stem extracts studied.

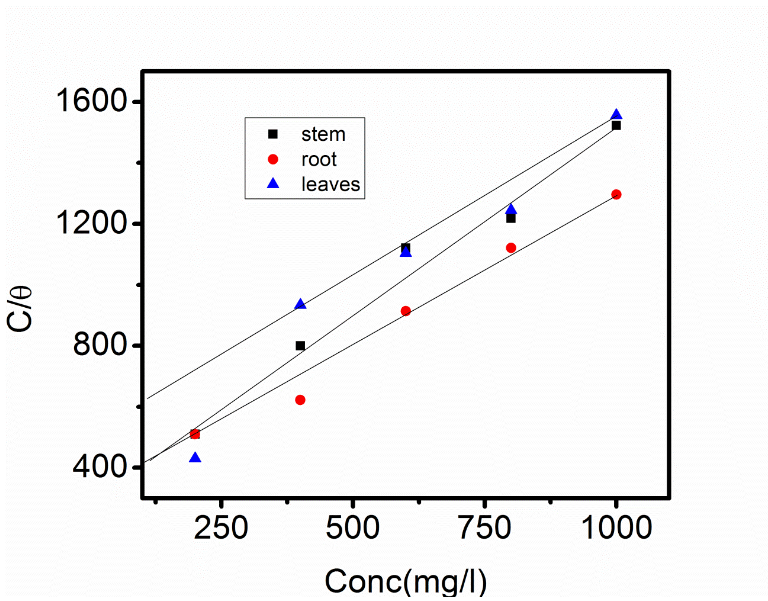

Figure 3: **Langmuir Isotherm**

The relationship between the degree of surface coverage (θ) and *senna alata* leaves, root and stem extracts can be represented by the langmuir adsorption isotherm

$$\frac{C}{\theta} = C + \frac{1}{k_{ad}} ----------------- 5$$

Where K is the constant for adsorption which is related to the free energy of adsorption (ΔG^0_{ad}) by equation 6

K = $\frac{1}{55.5}$ exp ($\frac{\Delta G^{0}_{ad}}{RT}$) -- 6

ΔG_{ad} is change in free energy of adsorption, R is universal gas constant, T is temperature of the system studied, C and θ are concentration of the extract and degree of surface coverage respectively. Figure 3 shows a plot at C/θ against concentration of *Senna alata* leaves, stem and root extracts in 1M HCl studied to be linear with intercept 1/k which suggest that the experiment fits into Langumuir adsorption isotherm. The calculated values of ΔG_{ad} are shown in tables 1 and 2. The negative sign indicates that *Senna alata* leave, root and stem extracts were spontaneously adsorbed to the surface of the mild steel in acidic medium studied. (12, 33-38).

Table 1: **Results of free energy of adsorption of *Senna alata* Leaves, Stem and Root Extract in Concentrations studied at 303K**

System (mg/l)	ΔG^{o}_{ad} Kj (Stem)	ΔG^{o}_{ad} Kj (Leaves)	ΔG^{o}_{ad} Kj (Root)
200	-58.05	-55.04	-58.04
400	-60.62	-63.54	-54.69
600	-63.29	-62.97	-58.16
800	-61.07	-61.70	-58.41
1000	-63.33	-63.96	-57.57

3.4 EFFECT OF TEMPERATURE

Temperature has a significant influence on metal corrosion rates 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 the inhibition efficiency decreases as temperature rises, and adsorption is said to be physical while increase in inhibition efficiency as temperature rises indicates chemisorptions. In order words chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached (4, 12-15, 33-38)

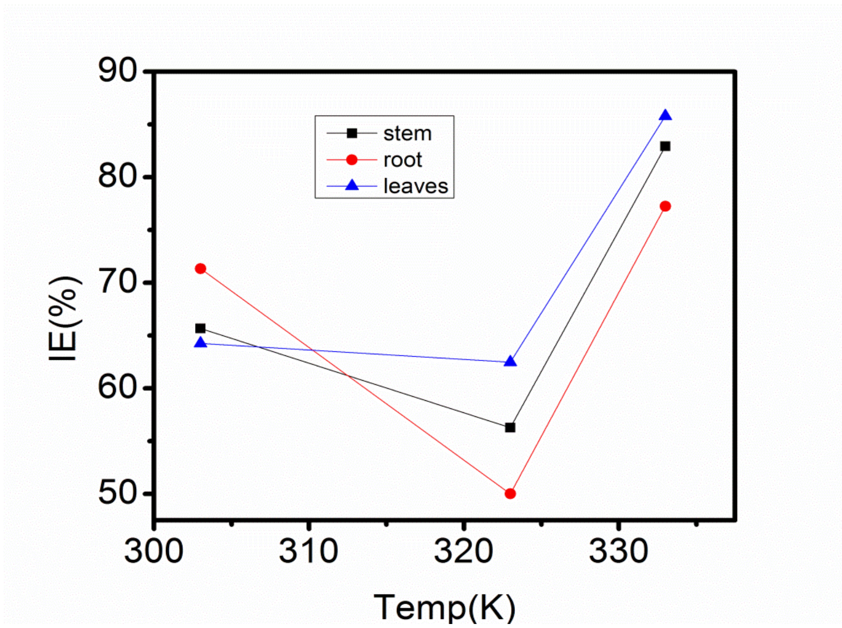

Figure 4: Inhibition Efficiency against Temperature of the System.

Figure 4 illustrates the effect of change in temperature on inhibition efficiency of *Senna alata* leaves stem and root extracts on corrosion of mild steel in 1M HCl. Inhibition efficiency in all the plant extracts studied (root, stem and leaves) showed evidence of decrease as temperature rises between 303K and 323K which can be attributed to physisorption mechanism, this observation can be explained with respect to the characteristic features of the ca thodic process of hydrogen evolution where the decrease of the reaction with rise in temperature leads to an increase in the rate of the cathodic reaction (17). This effect far overshadows the adsorption and inhibitive effect of *Senna alata*, because the enhanced rates of hydrogen gas evolution increasingly agitate the interface, which hinders inhibitor adsorption and also promotes dispersal of adsorbed inhibitor (12). Thus the marked reduction in inhibition efficiency with rise in temperature could be attributed to the shift of the adsorption desorption equilibrium towards desorption .(18 & 19) observations from the same figure 4 show a marked increase in inhibition efficiency as temperature increases between 323K to 333K. The increase in inhibition efficiency shows that molecules of *senna alata* leaves, root and stem extracts absorbed more on the metal surface as temperature increased from 50^0C to 60^0C, reducing the inherent reactivity of the metal at the sites where they are attached, and this behavior is evidence of chemisorptions mechanism (20).

3.5 Thermodynamic Parameters

To confirm which mechanism of adsorption that was involved in the corrosion inhibition of *senna alata*, some thermodynamic parameters like heat of adsorption and activation energy are considered. The relation between corrosion rate and temperature is often expressed by the Arrhenius equation.

$$K = A \exp\left(-\frac{Ea}{RT}\right) \text{ --- } 7$$

Where E_a is the activation energy, A is the Arrhenius pre-exponential factor and R is the gas constant. Equation 7 can be further expressed as

$$\text{Log } \frac{CR_2}{CR_1} = \frac{E_a}{2.303RT} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \text{ ----------------------------------- } 8$$

Where CR_1 and CR_2 are the corrosion rates at temperatures T_1 and T_2 respectively other parameters retain their previous meanings. The apparent activation energies for mild steel coupons in absence and presence of *senna alata* (leaves, stem and root) extracts were evaluated using equation 8 above. The apparent activation energy is observed from table 2 to decrease in inhibited systems containing leaves, stem and root extracts of *senna alata,* such behavior coupled with increase in inhibition efficiency with increase in temperature is evidence of chemisorptive interaction between the extract specie and mild steel surface. (5, 21 and 22). The drop in activation energy can be suggested to result from part of the energies being used for bond formation.

Table 2: Presentation of Activation Energy, Heat of Adsorption, and Free Energy

System (mg/l)	Ea (Kj)	ΔG(Kj) at 323K	ΔG(Kj) at 333K	ΔG^o_{ad} (Kjmol^{-1})
800 (Stem)	142.64	-65.08	-20.50	6.09 X 10^{-7}
800 (Root)	165.80	-67.63	-5.60	5.60 X 10^{-7}
800 (Leave)	138.12	-62.47	-49.44	5.90 X 10^{-7}
Blank	284.66			

Heat of adsorption (Q_{ad}) is related to the surface coverage through the relation in equation 9.

$$Q_{ad} = 2.303R \ [\log(\frac{\theta_2}{1-\theta_2}) - \log(\frac{\theta_1}{1-\theta_1})] \ x \ (\frac{1}{T_1} - \frac{1}{T_2}) \text{ -------------------- } 9$$

Where Q_{ad} is heat of adsorption, θ_1 and θ_2 are degrees of surface coverages at temperatures T_1 and T_2 respectively. The negative values of heat of adsorption are consistent of physisorption while the positive values are consistent of chemisorptions mechanism. (19 and 23) The calculated values of heat of adsorption shown also in table 2 are all positive which indicates physisorption mechanism. This confirms the earlier deduction made from results of apparent activation energy and temperature inhibition efficiency variation which indicated that *senna alata* leaves, stem and root extract were chemically absorbed to the metal surface, and the more efficient inhibitors appear to protect anodic sites preferentially by chemisorptions (16)

CONCLUSION

1. Extracts of *senna alata* leaves, stem and root each and respectively inhibited corrosion of mild steel in 1M HCl solution effectively
2. The inhibitive effect resulted from adsorption of *senna alata* leaves, stem and root extracts on mild steel surface fitting into Langmuir isotherm.
3. Inhibition efficiency generally increased with concentrations of the extract
4. Inhibition efficiency also increased with temperature suggesting chemisorptions mechanism, which was confirmed by corresponding values of apparent activation energies and heat of adsorption derived from corrosion rate and degree of surface coverage.

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