

Inhibitive action and adsorption characteristics of *Alternanthera bettzickiana* extracts on the corrosion of mild steel in acidic media

ABSTRACT

The inhibitive action of leaves, stem and root extracts of *Alternanthera bettzickiana* on mild steel corrosion in 5 M H₂SO₄ solutions was studied using gravimetric technique in the temperature range 30 °C to 60 °C. Maximum inhibition efficiency (and surface coverage) was obtained at an optimum concentration. However, increase in temperature decreased the inhibition efficiency at the temperature range studied. The experimental data complied with the Langmuir, Freundlich and Temkin adsorption isotherm and the value and sign of the Gibb's free energy of adsorption obtained suggested that inhibitor molecules have been spontaneously adsorbed onto the mild steel surface through a physical adsorption mechanism. Thermodynamic parameters revealed that the adsorption process is spontaneous.

Keywords: Corrosion, *Alternanthera bettzickiana*, Inhibition Efficiency, Mild Steel, Adsorption

1. INTRODUCTION

Corrosion of metals/alloys, which can be defined as the deterioration or disintegration of materials due to their reaction with the environment, has continued to receive attention in the technological world. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [1]. Use of hazardous chemical inhibitors is totally reduced because of environmental regulations. Chromates, phosphates, molybdates etc. and a variety of organic compounds containing heteroatom like nitrogen, sulphur and oxygen have been investigated as corrosion inhibitors [1-6]. Recently, due to increasing environmental awareness and the need to develop environmentally friendly processes, attention has been focused on the corrosion inhibiting properties of natural products of plant origin. This area of research is of much importance because in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable sources of materials. The present study investigates the inhibiting effect of leaves, stem and root extracts of *Alternanthera bettzickiana* on mild steel corrosion in 5 M H₂SO₄ solutions using the weight loss technique. *Alternanthera bettzickiana* is an herbaceous perennial plant, often with variegated leaves, growing 20 – 80 cm tall [7]. The preliminary study of the pharmaceutical constituent of *Alternanthera bettzickiana* showed that it is useful in purifying and nourishing blood. It is also claimed to be a soft laxative, a galactagogue and an antipyretic in addition to its wound healing property.

2. EXPERIMENTAL DETAILS

The Mild steel was bought from Artsian Market Enugu; Nigeria was used for the investigation. Mild steel of 1mm thickness was used. It was mechanically cut into coupon of 4.0 cm × 2 cm. A small hole was drilled at one end of the coupon for easy hooking. The coupon was mechanically polished with series of Aluminum oxide emery papers of grade no's 60, 80, 240, 400 and 600, washed thoroughly with distilled water and degreased with ethanol and dried with acetone and finally stored in desiccators.

2.1 Preparation of Plant Extracts

The leaves, stem and root of *Alternanthera bettzickiana* were collected from Nnamdi Azikiwe University, Awka Nigeria. 60 g of ground stem of *Alternanthera bettzickiana*, were taken into different 1000 ml round bottom flask and enough quantity of ethanol was added as solvent for extraction. The round bottom flask was covered with stopper and left for 24 hrs. Then the resultant extract was filterer and the solvent was evaporated in thermostate water bath at 70 °C by concentrating the extract to 20 %. 7.5 g of the ethanol stem extract were added in 1000 ml of 1 M and 5 M H₂SO₄ and left to cool for 24 hours. The resultant solution was filtered and stored in a 1.0 L volumetric flask. From the stock solution (7.5 g/L), inhibitor test solutions (concentrations of 0.5, 1.0, 2.5 and 5.0 g/L) were prepared.

2.2 Phytochemical Screening

Phytochemical analysis of the ethanol extract of leaves, stem and root of *Alternanthera bettzickiana* were carried out as described in literature [8, 9].

2.3 Gravimetric Method (Weight Loss)

The weighed mild steel coupons were suspended in beakers containing 100 ml of the test solution at room temperature. The mild steel coupons were completely immersed in the test solutions and retrieved every hour for 1-5 times.

The retrieved coupons were washed, scrubbed with bristle brush under fast flowing water, rinsed in ethanol, dried using acetone, re-weighed and re-immersed in the corrosive [10, 11]. The weight loss of the mild steel was evaluated in grams as the difference in the initial and final weight of the coupons. The experiment was carried out for the *Alternanthera bettzickiana* leaves, stem and root extracts using concentrations of 0.5 g/L, 1.0 g/L, 2.5 g/L, 5.0 g/L and 7.5 g/L at 30 °C, 40 °C and 60 °C. From the weight loss data, the corrosion rates (CR) were calculated from equation below.

$$CR (g \text{ cm}^{-2} \text{ hr}^{-1}) = WL/AT$$

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Where; WL= weight loss

A= specimen surface area

T= the period of immersion in hours

From the corrosion rate, the surface coverage (Θ) as a result of adsorption of inhibitor molecules and inhibition efficiencies of the molecules (I %) were determined using equation respectively;

$$\Theta = (CR_{Blank} - CR_{In})$$

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 CR_{Blank}

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$$I \% = \frac{(CR_{Blank} - CR_{inh})}{CR_{Blank}} \times 100$$

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 CR_{Blank}

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Where CR_{Blank} and CR_{inh} are the corrosion rates in the absence and presence of the plant extracts respectively.

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3. RESULTS AND DISCUSSION

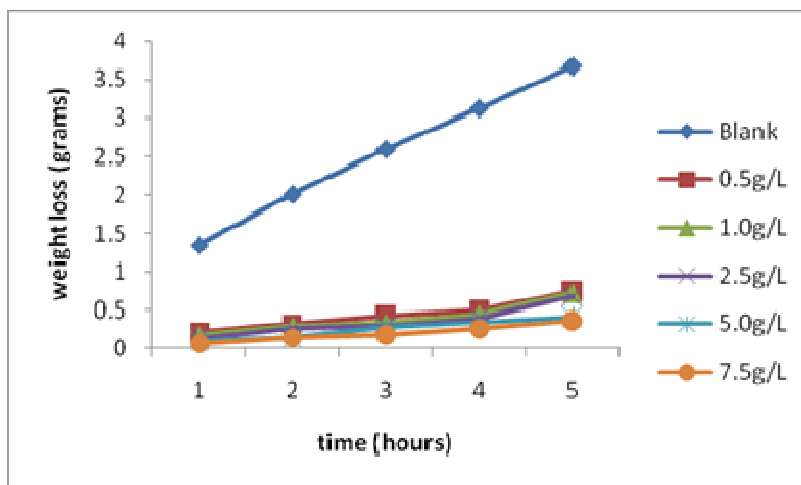
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3.1 Gravimetric Analysis

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The weight losses (gravimetric measurements) for the mild steel in 5 M H_2SO_4 containing different concentrations of the leaves, stem and root extracts of *Alternanthera bettzickiana* as a function of time, 1-5 hours' immersion time are presented at 30 °C, 40 °C and 60 °C in Figure 1-9, respectively. The results show that weight losses increase with increase in time but decrease with increase in concentration of the plants extracts. The decrease is due to the inhibitive effects of the leaves, stem and root extracts of *Alternanthera bettzickiana* and these effects increase with increase in *Alternanthera bettzickiana* concentration. And also as weight loss of the mild steel increases as the temperature increases. From the weight loss data, the corrosion rates (CR) were calculated.

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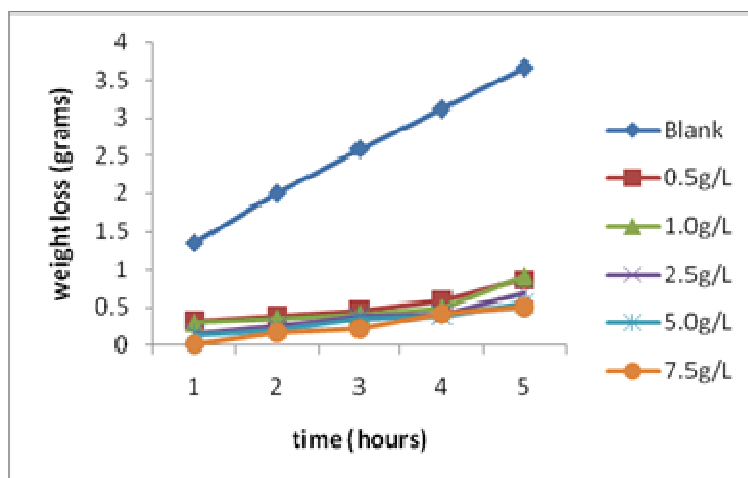


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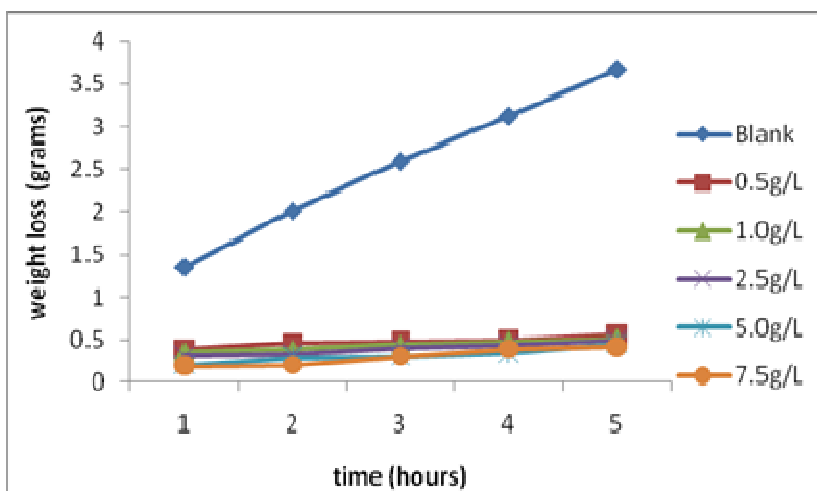
Fig :1 variation of weight loss with time for mild steel corrosion in 5 M H_2SO_4 in the presence and absence of ethanol extract of *Alternanthera bettzickiana* leaves at 30 °C.

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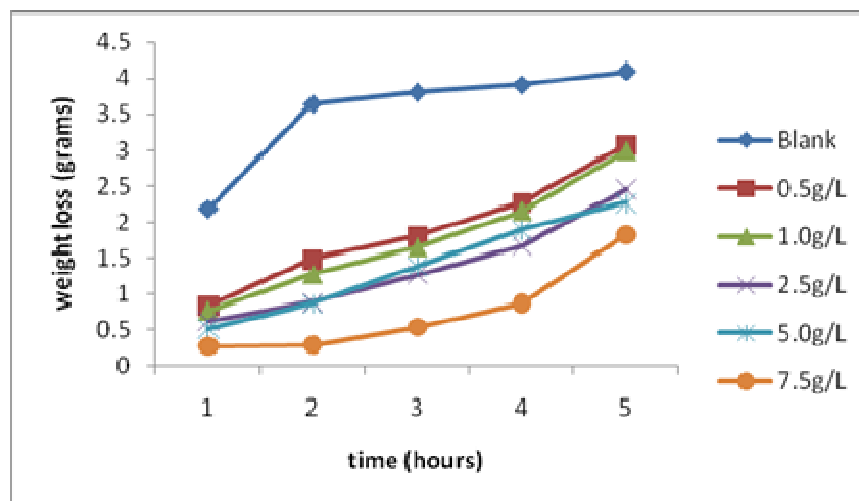
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103 **Fig 2: variation of weight loss with time for mild steel corrosion in 5 M H₂SO₄ in the**
 104 **presence and absence of ethanol extract of *Alternanthera bettzickiana* stem at 30 °C.**



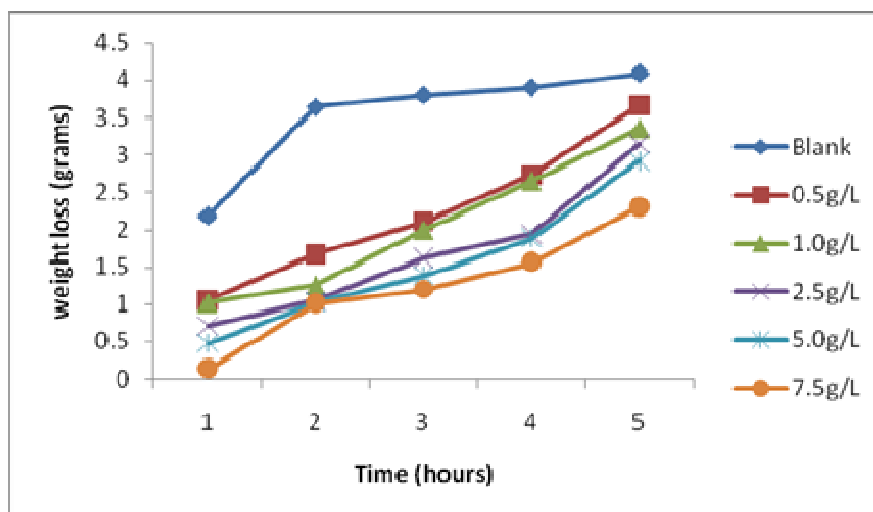
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106 **Fig 3: variation of weight loss with time for mild steel corrosion in 5 M H₂SO₄ in the**
 107 **presence and absence of ethanol extract of *Alternanthera bettzickiana* root at 30 °C.**



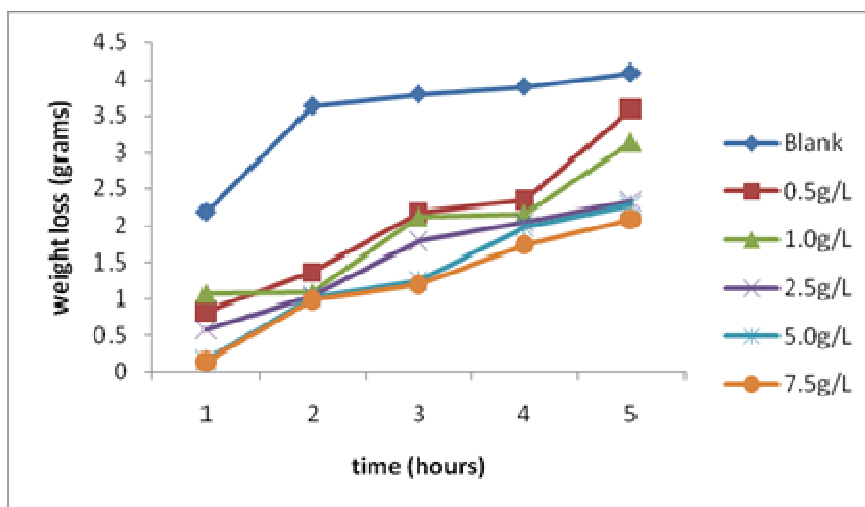
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109 **Fig 4: variation of weight loss with time for mild steel corrosion in 5 M H₂SO₄ in the**
 110 **presence and absence of ethanol extract of *Alternanthera bettzickiana* leaves at 40 °C.**



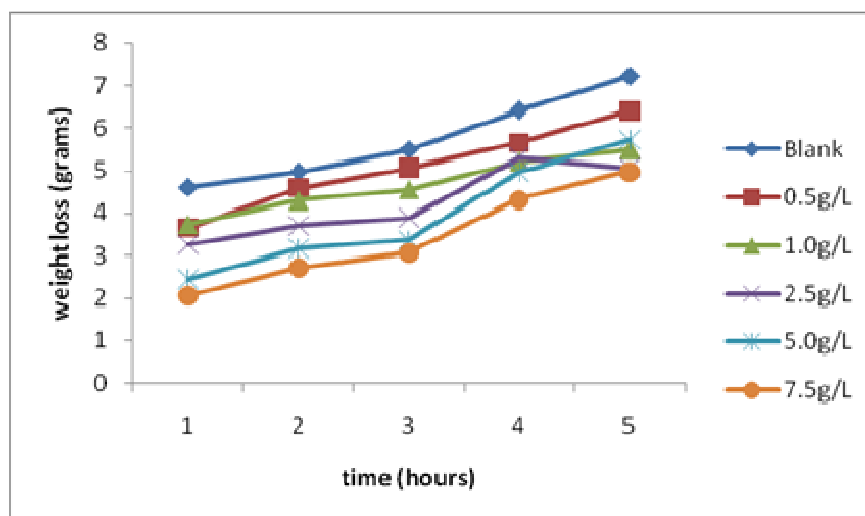
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112 **Fig 5: variation of weight loss with time for mild steel corrosion in 5 M H₂SO₄ in the**
 113 **presence and absence of ethanol extract of *Alternanthera bettzickiana* stem at 40 °C**



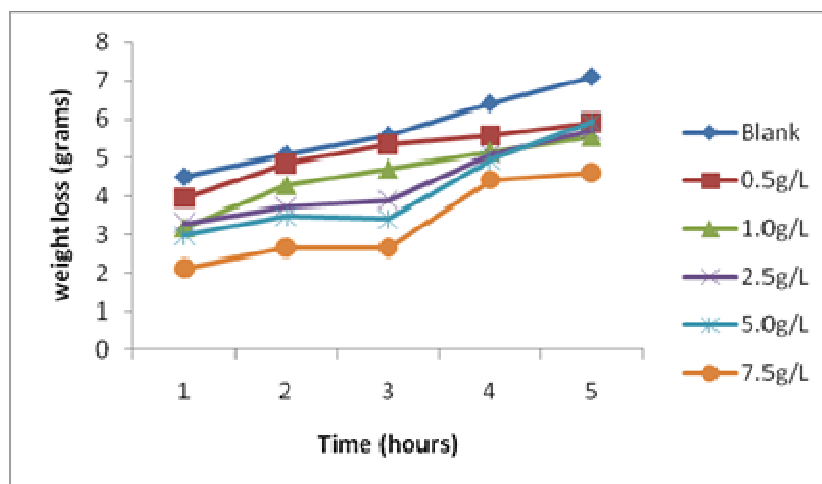
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115 Fig 6: variation of weight loss with time for mild steel corrosion in 5 M H₂SO₄ in the
116 presence and absence of ethanol extract of *Alternanthera bettzickiana* root at 40 °C.



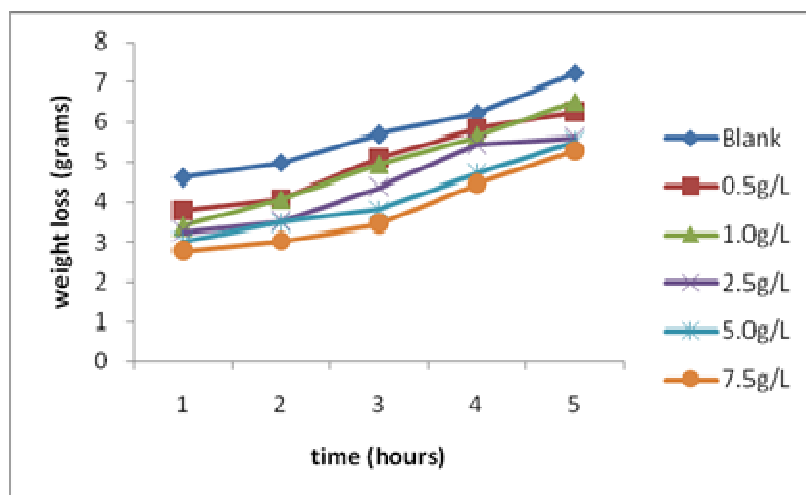
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118 Fig 7: variation of weight loss with time for mild steel corrosion in 5 M H₂SO₄ in the
119 presence and absence of ethanol extract of *Alternanthera bettzickiana* leaves at 60 °C.



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121 Fig 8: variation of weight loss with time for mild steel corrosion in 5 M H₂SO₄ in the
122 presence and absence of ethanol extract of *Alternanthera bettrockiana* Stem at 60 °C.



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124 Fig 9: variation of weight loss with time for mild steel corrosion in 5 M H₂SO₄ in the
125 presence and absence of ethanol extract of *Alternanthera bettrockiana* Root at 60 °C.
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Table 1: Inhibition Efficiency and corrosion Rate of Mild Steel in 5 M H₂SO₄ for different concentrations of *Alternanthera bettzickiana* leaves, stem and root extracts at different temperatures.

Inhibitor Conc	Inhibitor Efficiency (%)			Corrosion Rate (gcm ⁻² hr ⁻¹)		
	30 °C	40 °C	60 °C	30 °C	40 °C	60 °C
Blank				0.0296	0.0409	0.0668
Leaves						
0.5 g/L	82.6855	46.2784	11.6699	0.0051	0.0220	0.0590
1.0 g/L	84.6093	49.8296	18.7707	0.0046	0.0205	0.0542
2.5 g/L	86.1013	60.7955	24.8302	0.0041	0.0160	0.0502
5.0 g/L	90.2238	71.3352	31.4122	0.0029	0.0117	0.0458
7.5 g/L	92.0691	78.4034	40.1881	0.0023	0.0088	0.0399
Stem						
0.5 g/L	79.4660	36.1364	10.5520	0.0061	0.0261	0.0597
1.0 g/L	80.9580	41.6080	20.4771	0.0056	0.0239	0.0531
2.5 g/L	85.2768	52.0341	26.0665	0.0044	0.0196	0.0494
5.0 g/L	87.3106	56.3068	27.8948	0.0038	0.0179	0.0482
7.5 g/L	89.9568	64.7102	38.9866	0.0030	0.0144	0.0407
Root						
0.5 g/L	81.3899	41.3921	12.7669	0.0055	0.0240	0.0583
1.0 g/L	82.6855	45.8239	14.3479	0.0051	0.0222	0.0572
2.5 g/L	84.2167	55.1364	22.7407	0.0047	0.0184	0.0516
5.0 g/L	87.4755	62.0511	28.4869	0.0037	0.0155	0.0478
7.5 g/L	88.4178	65.0796	33.9892	0.0034	0.0143	0.0441

The inhibition efficiencies for each of the constituents shown in Table 1 revealed that the percentage inhibition efficiency increased with increase in concentration from each of the plant extract, that is, leaves, stems and roots. Table 1 showed that leaves extract gave the highest inhibition efficiency of 92.0619% followed by stem extract 88.9568 % and root extract 88.4178 % at the inhibitor concentration of 7.5 g/L. An increase in the concentration of each plant extract meant that the degree of surface coverage of the mild steel by the inhibitors would be increased, leading to increase in adsorption of the inhibitor molecules. This brings about increased inhibition efficiency. Considering the dependence of inhibition efficiency on the concentration as represented in table1, it seems to be possible that the inhibitor acts by adsorbing and blocking the available active centre for steel dissolution. In other words, the inhibitor decreases the active centre for steel dissolution. The adsorption process is made possible due to the presence of heteroatom such as O which is regarded as active adsorption centre.

Decrease in inhibition efficiency with increase in temperature may be attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of the metal that may otherwise inhibit the reaction. Ergun has attributed the inhibition efficiency decrease with rise in temperature to be due to an enhanced effect of temperature on the dissolution process of steel in acidic media and/or the partial desorption of the inhibitor from the metal surface [12]. A similar trend has been reported in [13]. As far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitors at the metal/aggressive solution interface is the first step in the inhibition mechanism [14].

The results obtained Tables 1 showed that the rate of corrosion of mild steel decreased with increase in the concentration of *Alternanthera bettzickiana* leaves, stem and root extracts but increased with increase in temperature.

3.2 Kinetics Studies

In this study, $\log (W_o/W_t)$ was plotted against time (in hours), and a linear variation was observed, which confirms a first-order reaction kinetics with respect to mild steel in H_2SO_4 solutions, formulated as:

$$\text{Log } W_t = \text{Log } W_o - kt \quad (4)$$

Where W_o is the initial weight before immersion, W_t weight after immersion at time t , k is the rate constant and t is time. The values of the rate constants, k , obtained from the slopes of the plot of $\log (W_o/W_t)$ against time (in hours) and the half-life, $t_{1/2}$, are presented in Table 2:

Table 2: Values for the rate constant and half life

	30 °C		40 °C		60 °C	
	K	$t_{1/2}$	K	$t_{1/2}$	K	$t_{1/2}$
Leaves						
Blank	0.067	10.343	0.052	13.327	0.326	2.125
0.5 g/L	0.010	69.300	0.049	14.143	0.178	3.893
1.0 g/L	0.011	63.000	0.048	14.438	0.096	7.219
2.5 g/L	0.009	77.000	0.039	17.769	0.095	7.295
5.0 g/L	0.007	99.000	0.034	20.382	0.110	6.300
7.5 g/L	0.005	138.60	0.026	26.654	0.107	6.477
Stem						
Blank	0.067	10.343	0.052	13.327	0.326	2.125
0.5 g/L	0.008	86.625	0.060	11.550	0.110	6.300
1.0 g/L	0.011	63.000	0.055	12.600	0.112	6.188
2.5 g/L	0.009	77.000	0.050	13.860	0.129	5.372
5.0 g/L	0.008	86.625	0.048	14.438	0.142	4.880
7.5 g/L	0.010	69.300	0.036	19.250	0.091	7.615
Root						
Blank	0.067	10.343	0.052	13.327	0.326	2.125
0.5 g/L	0.002	346.50	0.063	11.000	0.155	4.471
1.0 g/L	0.003	231.00	0.054	12.833	0.228	3.039
2.5 g/L	0.003	231.00	0.036	19.250	0.155	4.471
5.0 g/L	0.004	173.25	0.039	17.769	0.124	5.589
7.5 g/L	0.004	173.25	0.034	20.382	0.107	6.477

3.3 Adsorption and Thermodynamic Studies

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals has been deduced in terms of adsorption characteristics of the inhibitor. The decrease in the corrosion rate by the addition of aqueous extract of *Alternanthera bettizickiana* leaves, stem and root is attributed to either adsorption of the plant components on the metal surface or, the formation of a barrier film separating the metal surface from the corrosive medium [15], and this is usually confirmed from the fit of the experimental data to various adsorption isotherms. Several adsorption isotherms were tested for fit with the experimental data.

185 These include the Langmuir, Freundlich and Temkin isotherms. The Langmuir, Freundlich
186 and Temkin are given by the expression in 4,5 [16] and 6 [17]

$$\begin{array}{ll} 187 & \\ 188 & C/\Theta = 1/K_{\text{ads}} + C \quad 4 \\ 189 & \text{Log } \Theta = \text{Log } K_f + n\text{Log}C \quad 5 \\ 190 & \Theta = -1/2a\ln C - 1/2a\ln K_{\text{ads}} \quad 6 \\ 191 & \end{array}$$

192 Where Θ is the degree of surface coverage, 'a' is a molecular interaction parameter whose
193 value depends on the type of molecular interactions in the adsorption layer and the degree
194 of homogeneity of the surface, C is the inhibitor concentration while K_{ads} and K_f is the
195 adsorption equilibrium constant which is temperature dependent.

$$\begin{array}{ll} 196 & \\ 197 & \Delta G_{\text{ads}}^{\circ} = -RT\ln(55.5 \times K_{\text{ads}}) \quad 7 \end{array}$$

198 Where $\Delta G_{\text{ads}}^{\circ}$ is the standard free energy of adsorption, R, is the molar gas constant and T
199 is absolute temperature.

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201 The Langmuir, Freundlich and Temkin adsorption parameters in the presence of
202 *Alternanthera bettzickiana* leaves, stem and root extracts in 5 M H_2SO_4 are presented in
203 Tables 3, which showed that all the linear correlation coefficients (R^2) are almost equal to 1
204 and the slopes are close to 1, which confirmed that the adsorption of the plant extracts on
205 mild steel surface obeyed Langmuir, Freundlich and Temkin adsorption isotherm. Tables 3
206 revealed that K_{ads} decreased with increasing temperature, which indicated that the plant
207 extract is easily and strongly adsorbed onto the mild steel surface at lower temperature,
208 however, the adsorbed extract tended to desorb from mild steel surface at higher
209 temperatures, suggesting that the inhibitors are physically adsorbed on the surface of the
210 mild steel [18].

211 The Positive values of 'a' indicates attraction forces between adsorbed molecules while
212 negative values indicate repulsive forces between the adsorbed molecules [19]. It is seen in
213 the table 3 that the values of 'a' in all cases are negative indicating that repulsion exists in
214 the adsorption layer [19].

215 Generally, values of $\Delta G_{\text{ads}}^{\circ}$ around -20 kJ/mol or lower are consistent with the electrostatic
216 interaction between the charged molecules and the charged metal (physisorption); those
217 around -40 kJ/mol or higher involve charge sharing or charge transfer from organic
218 molecules to the metal surface to form a coordinate type of bond (chemisorption) [20, 21, 22,
219 23]. The calculated $\Delta G_{\text{ads}}^{\circ}$ value showed, therefore, that the adsorption mechanism of
220 *Alternanthera bettzickiana* leaves, stem and root extracts in 5 M H_2SO_4 on mild steel are
221 physically adsorbed.

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Table 3: The values of K_{ads} , ΔG°_{ads} and R^2 from the Langmuir, Freundlich and Temkin isotherms for mild steel in 5 M H_2SO_4 solution

Temperature (K)	Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm			a
	K_{ads}	ΔG°_{ads}	R^2	K_{ads}	ΔG°_{ads}	R^2	K_{ads}	ΔG°_{ads}	R^2	
Leaves										
30 °C	8.000	-15.356	0.999	0.845	-10.33	0.958	1.022	-10.865	0.948	-0.017
40 °C	1.259	-11.051	0.994	0.515	-9.007	0.986	1.064	-10.955	0.971	-0.060
60 °C	0.262	-7.411	0.969	0.169	-6.006	0.977	1.018	-10.834	0.965	-0.049
Stem										
30 °C	7.463	-15.181	0.999	0.817	-10.24	0.984	1.032	-10.871	0.983	-0.019
40 °C	1.051	-10.581	0.951	0.419	-8.450	0.988	1.044	-10.902	0.979	-0.051
60 °C	0.273	-7.525	0.940	0.166	-5.964	0.896	1.016	-10.830	0.915	-0.045
Root										
30 °C	10.30	-15.995	0.999	0.828	-10.28	0.963	1.022	-10.846	0.960	-0.013
40 °C	1.464	-11.444	0.998	0.466	-8.734	0.995	1.043	-10.901	0.995	-0.001
60 °C	0.168	-6.181	0.981	0.157	-5.815	0.983	1.013	-10.822	0.960	-0.040

Table 4: Thermodynamics parameter for adsorption of ethanol extract of 5 M H_2SO_4 *Alternanthera bettzickiana* Leaves, Stem and Root.

Conc	Leaves			Stem			Root		
	E_a	ΔH°	ΔS°	E_a	ΔH°	ΔS°	E_a	ΔH°	ΔS°
Blank	22.373	19.904	186.608	22.373	19.904	186.606	22.373	19.904	186.606
0.5 g/L	64.783	62.540	80.482	60.110	57.818	94.450	62.205	59.930	88.297
1.0 g/L	65.539	63.289	78.819	58.930	56.629	99.023	63.835	61.576	83.558
2.5 g/L	66.986	64.785	75.244	64.076	61.809	84.057	64.010	61.742	84.057
5.0 g/L	74.477	72.343	53.460	67.452	65.217	73.997	68.233	66.024	71.835
7.5 g/L	79.474	74.895	47.141	69.289	67.072	69.840	68.200	65.591	72.666

The apparent activation energies (E_a) for the corrosion process in absence and presence of inhibitor were evaluated from Arrhenius equation:

$$\ln K = (-E_a/RT) + \ln A \quad 8$$

Where E_a is the apparent effective activation energy, K is the corrosion rate, T is the absolute temperature, R is the universal gas constant, and A is Arrhenius pre-exponential factor.

It was observed that, there was a higher value of E_a in presence of the *Alternanthera bettzickiana* leaves, stem and root extracts in 5 M H_2SO_4 than in its absence and could be interpreted as an indication of adsorption effects. In presence of the inhibitor, the increased values of E_a , in general, reflected that the good ability to hinder the corrosion of mild steel in such conditions. In other words, the adsorption of the inhibitor on the mild steel surface leads to the formation of a physical barrier that reduces the metal reactivity in the electrochemical reactions of the corrosion.

An alternative formulation of the Arrhenius equation is the transition state equation were used to elucidate the mechanism of corrosion inhibition as given below [24]

$$K = [(RT)/Nh] [\exp(\Delta S^{\circ}/R)] [\exp(\Delta H^{\circ}/RT)] \quad 9$$

Where K is the corrosion rate, R the general gas constant, h is the plank's constant, N is Avogadro's number, ΔS^* is the apparent entropy of activation and ΔH^* is the apparent enthalpy of activation.

A plot of $\ln(K/T)$ vs. $1/T$ gave a straight line with the slope of $-\Delta H^*/R$ and the intercept of $\ln(R/Nh) + \Delta S^*/R$, from which the values of ΔS^* and ΔH^* were calculated as given in Table 4.

The computed values of the thermodynamic parameters of activation for the dissolution of mild steel at different temperatures are presented in Table 4. Examination of these results revealed that the values of enthalpy in the presence of the additives increase over that of the uninhibited solution. The positive values of enthalpy showed the endothermic nature of the dissolution process. The value of entropy in the presence and absence of the extracts is positive, meaning that an increase in disorder takes place in going from reactant to the activation complex [25]. In addition, as the adsorption was an endothermic process, it should have been accompanied by an increase in entropy [26].

Table 5: Showed the phytochemical composition of ethanol extracts of *Alternanthera bettzickiana* leaves, stem and root.

Phytochemical Result	Leaves	Stem	Root
Alkaloid	+	+	+
Flavonoid	+	+	+
Tannins	+	+	+
Steroids	+	+	+
Saponin	-	-	-
Glycoside	+	+	+

The phytoconstituents in the leaves, stem and root extracts contain an alkaloid, flavonoid, tannins, steroid and glycosides. It is revealed from the result that the Inhibition efficiency of *Alternanthera bettzickiana* leaves, stem and root extracts may be explained as due to the adsorption of these compounds on the metal surface thereby blocking the surface and protecting the metal from the aggressive atmosphere.

4.0 CONCLUSION

Results from the study shows that the ethanol extract of the leaves, stem and root of *Alternanthera bettzickiana* inhibited the corrosion of mild steel in H_2SO_4 medium. The presence of alkaloids, flavonoids, tannins, steroids and glycosides containing hetero-atoms like oxygen, sulphur and nitrogen in its molecules collaborates these observed results. At the inhibitor concentration of 7.5 g/l and at 30 °C, the leave extract gave the highest inhibition efficiency of 92.0619 % followed by stem extract 88.9568 % and root extract 88.4178 %. The inhibition efficiency increased with increasing inhibitor concentration and this suggested that the inhibitor molecules acted by adsorption on the metal surface. The negative values of the molecular interactions 'a' in the adsorption layer indicating that repulsion exists in the adsorption layer. The values of ΔG_{ads}^0 for *Alternanthera bettzickiana* leaves, stem and root extracts were less than -20 kJmol^{-1} indicating physical adsorption mechanism. The higher value of E_a in the presence of *Alternanthera bettzickiana* leaves, stem and root extracts compared to that in its absence and the decrease in the inhibition efficiency with rise in temperature is interpreted as an indication of physisorption.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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