Journal of Fundamental and Applied Sciences

ISSN 1112-9867

Available online at http://www.jfas.info

Research Article

MILD STEEL CORROSION INHIBITION IN ACIDIC MEDIA USING *SARCOCEPHALUS LATIFOLIUS* LEAVES EXTRACT

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Received: 17 October 2022 / Accepted: 28 March 2023 / Published: 29 March 2023

ABSTRACT

At temperatures between 303K and 323K, three different concentrations of the methanol extract from *Sarcocephalus latifolius* were utilized to inhibit the corrosion of mild steel coupons in a 0.9M HCl solution. The plant extract adhered to the surface of mild steel metal under the investigated conditions, according to surface characterization techniques including SEM and FT-IR. It has been proven through weight loss trials in this work that the plant extract's ability to suppress growth improves with both an increase in its concentration and a decrease in temperature. The corrosion and inhibition processes were presented as being viable and spontaneous using thermodynamic parameters. Additionally, it was determined that the inhibitory process followed first order kinetics, with half-life values rising as plant extract concentration did. Calculated activation energy values and isotherm characteristics demonstrated that the process adheres to the physical adsorption mechanism.

Keywords: Thermodynamics; Kinetics; Isotherms; Mild steel; Corrosion inhibition; *Sarcocephalus latifolius.*

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doi: http://dx.doi.org/10.4314/jfas.1277

1. INTRODUCTION

Researchers have given a great deal of attention to mild steel corrosion studies due to their significance in technology and practical uses[1-3]. This metal is utilized extensively in products including automobile, the aviation sector, home appliances, containers, and many electrical devices [4]. When producing some of these materials, alloys of other metals are added to increase their physical, aesthetical, and technological features, because using these metals alone in that applicable context would not fulfill the intended purpose [5]. The prolonged industrial usage of metals in corrosive settings typically promotes their oxidation and subsequently degrades their malleability, ductility, and conductivity properties, leading to the complete breakdown of the metal [5,6]. Important structures like bridges, oil pipelines, refineries, and buildings, among others, have always collapsed as a result of such failures, including structural, electrical, and mechanical ones [7].

Even though an alloy is made for a particular environment and a particular function, materials like mild steel can still corrode in hostile media [8]. One of the most important industrial chemicals for cleaning metals in procedures like acid pickling and electro polishing is hydrochloric acid, particularly in the oil industry where etching happens to some of the metals utilized [9]. Due to the acidic deposit on its surfaces, this causes erosion, corrosion, and other sorts of degradation [10]. Therefore, it is vital to look for inhibitors to prevent corrosion in this mild steel, a material with industrial applications. One of the most practical ways to prevent corrosion in acidic medium in industrial settings is to utilize inhibitors during the acid pickling process [5]. Organic compounds with hetero-atoms including oxygen, nitrogen, sulphur, and phosphorus, which enable molecule adsorption on metal surfaces, make up the majority of effective and efficient organic inhibitors. Due to their effectiveness and affordability, inhibitors have a significant industrial impact [11–13].

Numerous studies have examined various strategies for reducing or preventing corrosion on metal surfaces while taking into account the eco-friendliness of the inhibitors used. Recently, the use of pertinent compounds, the majority of which are heterocyclic in nature, as corrosion inhibitors has been accepted [8]. These compounds can be either existing chemicals or extracts from promising plant components. These compounds, which contain a variety of powerful phytochemicals, have been described as promising metal corrosion inhibitors when applied in tiny quantities to corrosive environments [13–15].

Using several experimental setups and procedures, the extract of *Sarcocephalus latifolius* leaves was employed in this study to prevent corrosion of mild steel coupons in 0.9M HCl aqueous media.

2. RESULTS AND DISCUSSION

2.1 Weight Loss Measurement

According to the results of the weight loss experiment shown in Table 1, the system's weight loss decreased as the concentration of the plant extract increased, and the system's corrosion rate also decreased as the concentration of the extract increased. This demonstrates the plant extract's ability to prevent corrosion on the metal's surface. The surface coverage was also found to rise with the increase in plant extract concentration; this is another sign of the plant extract's efficiency on the surface of mild steel. This outcome is consistent with that which Ayuba and Abdullateef [9] reported. The system's corrosion inhibition efficiency peaked at 303K with a value of 57.30% before declining somewhat at 313K with a maximum value of 44.21%, and eventually dropping to 38.03% at 323K. This suggests that the plant extract's ability to inhibit corrosion is temperature-dependent and that as the system's temperature rises, the effectiveness of the system's ability to inhibit corrosion reduces [11,14]. It can be deduced that a drop in temperature and an increase in plant extract concentration are connected to a decrease in corrosion rate and an increase in inhibitory efficiency of the examined extract, respectively [5,6].

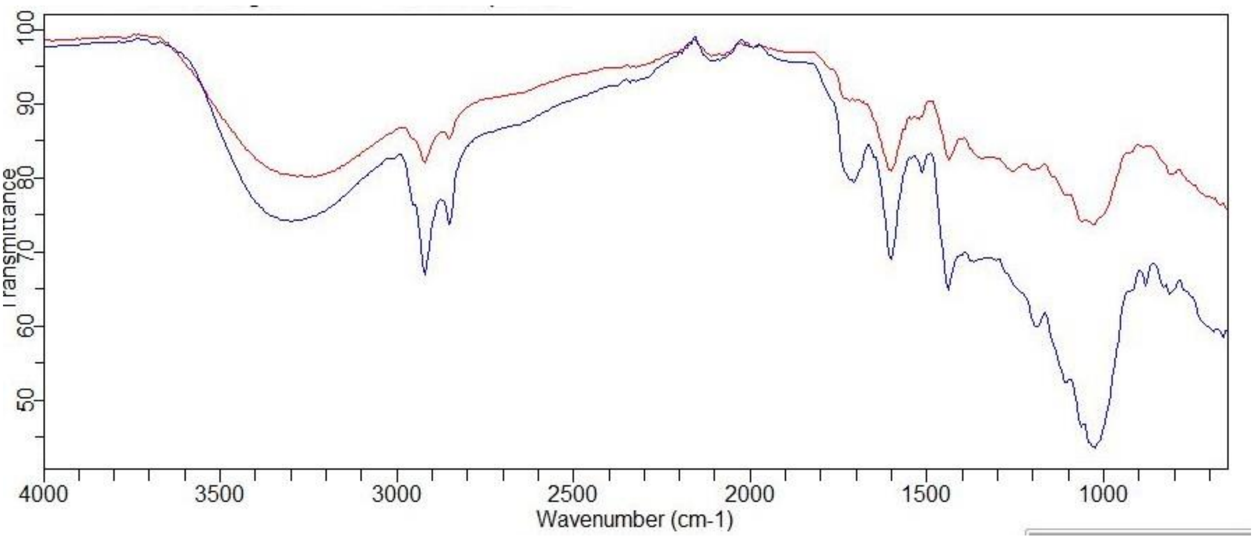
Table 1. Calculated parameters of the weight loss experiment

Temp (K)	Extract Conc. (g/L)	Δw (g)	CR ($g/cm^2.h$) × 10^{-3}	θ	I. E. (%)
303	0.0	0.0890	1.854	-	-
	0.2	0.0580	1.208	0.3483	34.83
	0.4	0.0470	0.979	0.4719	47.19
	0.6	0.0370	0.792	0.5730	57.30
313	0.0	0.1192	2.483	-	-

	0.2	0.0905	1.885	0.2408	24.08
	0.4	0.0855	1.781	0.2827	28.27
	0.6	0.0665	1.385	0.4421	44.21
323	0.0	0.2085	4.344	-	-
	0.2	0.1775	3.694	0.1496	14.96
	0.4	0.1522	3.171	0.2706	27.06
	0.6	0.1292	2.692	0.3803	38.03

2.2 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups that are present in the methanol extract of *Sarcocephalus latifolius* as well as the extract that forms a corrosion-protective coating on the surface of mild steel were identified using the FTIR method. Figure 1 displays the *Sarcocephalus latifolius* extract's infrared spectrum superimposed with the spectrum of the extract following adsorption. Corrosion is shown by the red and green lines, respectively. It is possible to see a shift in band locations on the spectrum by comparing the absorption bands spectra of the inhibitor *Sarcocephalus latifolius* before and after corrosion. 3301 to 3316 cm^{-1} (-OH stretching), 1701 cm^{-1}with only an intensity change (-C=O stretching), 1603 cm^{-1} to 1622 cm^{-1} (C=C), and 1103 cm^{-1} to 1622 cm^{-1} (C-O stretching), among others without a shift change, have a shift change in the intensity [11-15]. The adsorption and interaction of various functional groups of the extract of *Sarcocephalus latifolius* leaves on the metallic surface are shown by the shifted absorption bands mentioned above [11]. The interaction of the inhibitor on the metallic surface as adsorption in corrosion inhibition in HCl is revealed by the FTIR surface analysis, which shows that functional groups contained in the extract, such as -OH, -COOH, -C=C, =N-H, -C=N, and C=O, are engaged in the process [9-11].

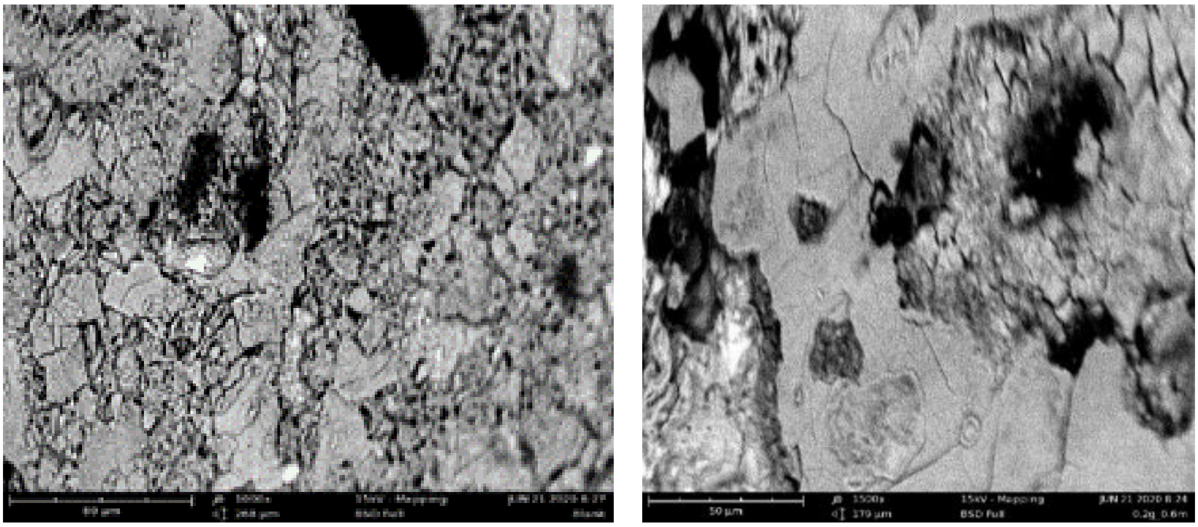


***Key:** red line (plant extract after corrosion) and green line (plant extract before corrosion)*

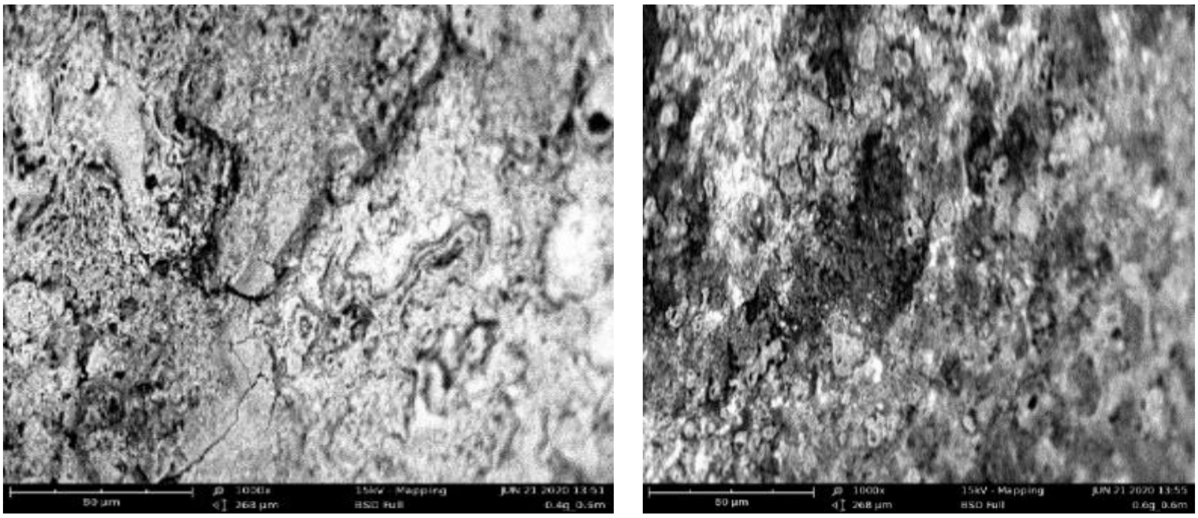
Fig.1. FTIR spectra of *Sarcocephalus latifolius* leaves extract before and after mild steel corrosion

2.3 Scanning Electron Microscopy (SEM)

SEM analysis was performed on the surface of the mild steel in 0.9M HCl both before and after the addition of the plant extract at various doses. The goal of this is to identify any potential morphological alterations brought on by the addition of plant extract. The blank was discovered to be rough from the micrographs shown in Figure 2, with cracks and patches clearly visible revealing the action of 0.9M HCl on the surface of the mild steel. The smoother metal surface was seen when this was compared to that containing the plant extract at varied concentrations of 0.2g/L, 0.4g/L, and 0.6g/L, with the holes and surface fracture gradually going away as the concentration of the extract increases. This shows that the plant extract was applied to the surface of the mild steel, making the surface fractures and holes progressively disappear and protecting the metal's surface from corrosion [4,12].



Blank **0.2g**



0.4g **0.6g**

Fig.2. Micrograph of the mild steel surface before and after plant extract interaction

2.4 Adsorption Isotherm Studies

Adsorption isotherms are also utilized to foretell how plant extract and the surface of mild steel metal will interact [11–13]. Utilizing the adsorption parameter, surface coverage (θ), and inhibitor concentration, numerous isotherms were used to characterize the nature and effectiveness of the covering of inhibitors on the surface of metals. Temkin, Langmuir, and Freundlich adsorption isotherms were used in this study to analyze the adsorption effect of the plant extract on mild still in 0.9M HCl. With its R^2 value in Table 3 being relatively better than those of the other isotherms evaluated across all concentrations of the plant extract, the

Freundlich isotherm was the best fit for the corrosion inhibition of *Sarcocephalus latifolius* leaves extract on the mild steel in the medium [12–16]. According to Ayuba and Abubakar [11], the isotherms shown in Figure 3 with the highest R^2 values can be deemed to correspond with the experimental data and are subsequently determined to provide an explanation for the mechanism of the adsorption process. The most suited adsorption isotherm, according to Freundlich, can also be presented as a physical adsorption mechanism for the adsorption process [11]. Equation 1 gives a broad description of the two isotherms, while Table 2 gives the specific expressions of each isotherm in conversional and linear forms, respectively.

$$f(\theta, x) exp^{-2a\theta} = K_{ads} C_{inh} \qquad (1)$$

Table 2. The isotherms equations use for the corrosion studies

Isotherm	Conversional form	Linear form
Freundlich	$\theta = K_{ads}(C_{inh})^n$	$log\ \theta = nlog\ C_{inh} + log\ K_{ads}$
Langmuir	$\frac{\theta}{1-\theta} = K_{ads}\ C_{inh}$	$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$
Temkin	$exp^{(\theta - K_{ads})} = C_{inh}$	$\theta = lnC_{inh} + K_{ads}$

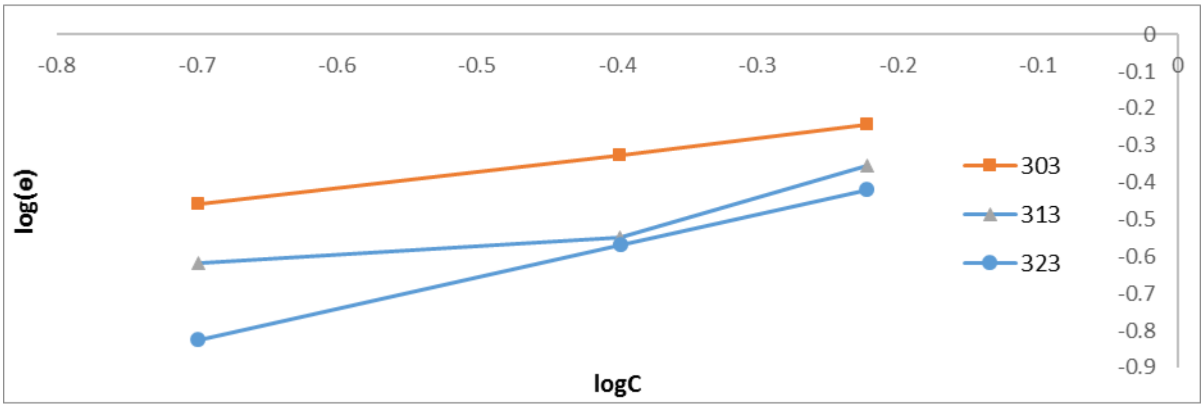


Fig.3. Freundlich isotherm for adsorption of *Sarcocephalus latifolius* on mild steel in 0,9M HCl

The values of K_{ads} obtained from the intercept of Freundlich adsorption isotherm plot was used to calculate the adsorption Gibb's free energy (ΔG_{ads}) using equation 2 [12].

$$\Delta G_{ads} = -RT ln(55.5 K_{ads}) \qquad (2)$$

Where 55.5M is the concentration of water in solution, T is the absolute temperature, and R is the molar gas constant.

Table 3 displays calculated ΔG_{ads} values for the adsorption process. The inhibitor's spontaneous and practical adsorption on the surface of mild steel is indicated by the negative values of ΔG_{ads} that were obtained. The fact that ΔG_{ads} values at all temperatures were less than -40 kJ/mol indicated that physical adsorption is the mechanism by which *Sarcocephalus latifolius* extract is inhibited on mild steel metal surface [17–19]. Freundlich's comparatively low values of ΔG_{ads} serve as another evidence of its greater energy stability.

Table 3. Isotherms values of *Sarcocephalus latifolius* on mild steel in 0.9M HCl at different temperatures

Isotherm	**Temperature (K)**	**Slope**	**ΔG_{ads} (kJmol^{-1})**	**R^2**	**K_{ads}**
Langmuir	303	1.18	-12.765	0.9919	2.86
	313	1.32	-11.479	0.6687	1.48
	323	0.60	-10.245	0.9866	0.82
Freundlich	303	0.45	-9.287	0.9994	0.72
	313	0.52	-8.781	0.8368	0.52
	323	0.85	-9.359	1.0000	0.58
Temkin	303	4.96	-18.471	0.9915	27.50
	313	5.88	-18.015	0.7909	18.26
	323	4.85	-16.983	0.9845	10.04

2.5 Kinetic Studies

By fitting the kinetic data from the weight loss experiment into various kinetic equation models, including zero, first, and second orders, the kinetics of mild steel corrosion in 0.9M HCl solution and its suppression with the plant extract were explored. The first order kinetics was determined to have the greatest values of the indicated parameters in Table 4 and to best suit the kinetic experimental data based on the reported values of R^2, rate constant (k), and half-life ($t_{1/2}$) [17-19]. Equation 6 derived from equation 3, which is how the first order kinetic equation is employed. When the starting weight of the mild steel, a_o, is taken into account together with the corrosion weight loss, x, and the weight loss difference at time t, w, the kinetic equation of the reaction can be given as follows:

$$\frac{dx}{dt} = k_1 (a_o - x) \tag{3}$$

Rearranging equation 3 produces equation 4 and upon integration of equation 5 yielded equation 6 respectively. From the equations derived k_1 is the first order rate constant.

$$dx/(a_o - x) = k_1\, dt \tag{4}$$

$$-ln(a_o - x) = k_1\, t \tag{5}$$

$$-log\ (\Delta w) = \frac{k_1 t}{2.303} \tag{6}$$

The half-life equation is obtained by fitting the value of the k_1 constant in to the half-life equation as shown in equation 7.

$$t_{1/2} = \frac{0.693}{k_1} \tag{7}$$

The values of the kinetic parameters determined from the graphs are shown in Table 4 as a plot of -log (Δw) on the vertical axis against time, t on the horizontal axis. Equation 8 was used to get the value of k_o for the zero order kinetics, and equation 9 was used to determine the relationship for the second order kinetics. Equation 9 was used to display the graph of 1/w against time(t) and get the value of k_2 [18].

$$w_o = w + k_o t \tag{8}$$

$$\frac{1}{w} = \frac{1}{w_o} + k_2 t \tag{9}$$

Where w is weight loss at time t and w_o is the initial weight of the coupon metal, k_o and k_2 are the rate constants for zero and second order kinetics respectively.

Table 4. Kinetic parameter values for the adsorption of the plant extract on mild steel in 0.9M HCl

	Zero order			1st order			2nd order		
Conc. (g/L)	R^2	k_0 (mol/Lhr^{-1})	$t_{1/2}$ (day)	R^2	k_1 (hr^{-1})	$t_{1/2}$ (day)	R^2	k_2 (mol/L)$^{-1}$(hr^{-1})	$t_{1/2}$ (day)
0.0	0.580	0.028	1.046	0.889	0.100	0.289	0.695	0.173	0.167
0.2	0.602	0.021	1.395	0.852	0.101	0.287	0.781	0.126	0.188
0.4	0.607	0.018	1.641	0.910	0.099	0.293	0.742	0.096	0.299
0.6	0.600	0.016	1.839	1.000	0.098	0.295	0.745	0.090	0.321

2.6 Effect of Temperature

Table 1's results revealed that weight loss values increase when system temperature rises from 303 to 323 K, which lowers the effectiveness of corrosion inhibition and the surface covering. This suggests that the mechanisms depend on temperature [19]. The expressions in equations 10 (Arrhenius) and 11 (Eyring) were used to verify the behavior of the process with respect to temperature and parameters including: entropy change of adsorption (ΔS_{ads}), enthalpy change of adsorption (ΔH_{ads}), and activation energy of adsorption (E_a) of the corrosion or corrosion inhibition effect of the extract were evaluated [9-11]. This helped to further explain how temperature affects the inhibition of the corrosion of mild.

$$logCR = logA - \frac{E_a}{2.303RT} \quad (10)$$

$$log\frac{CR}{T} = \left[\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{2.303R}\right)\right] - \frac{\Delta H}{2.303RT} \quad (11)$$

LogCR (corrosion rate) against 1/T was plotted in Figure 4 against, a slope that is similar to $-E_a/2.303R$. This slope was analyzed to determine E_a (the system's activation energy) and the values shown in Table 4. Equation 11 was also used to generate the ΔH_{ads} values from the slope and ΔS_{ads} values from the intercept in Figure 5, and the results are likewise shown in Table 4. According to the findings in Table 4, adding plant extract to the system raises its activation energy, and the activation energy rises as plant extract concentration rises. This shows that more energy is required with plant extract to overcome the activation energy before corrosion can happen. Since the blank's activation energy was relatively low, corrosion was easier to develop and more likely to occur there. Figure 4 depicts the Arrhenius equation plot to illustrate the impact of changing the concentration of the plant extract. The decrease in the negative values of entropy is a clear indication that the inhibitor was effective as the values in Table 4 of entropy decrease with the increase in concentration of the extract [20-22]. The change in entropy and the enthalpy of the system indicated that there was more orderliness in the system when the inhibitor concentration was introduced. The activated complex in the rate-determining step exhibits association rather than dissociation steps, which indicates that there was a decrease in disorderliness from the reactants to the activated complex formations, as seen by the negative values of entropies [23].

Table 5. The values of E_a, ΔH_{ads} and ΔS_{ads} of the corrosion inhibition of mild steel in 0.9M HCl

Extract conc. (g/L^{-1})	**ΔHads (kJmol^{-1})**	**Ea (kJmol^{-1})**	**ΔSads (JK^{-1})**
0.0	31.912	34.515	-0.1925
0.2	42.753	45.356	-0.1602
0.4	45.206	47.809	-0.1535
0.6	47.134	49.737	-0.1490

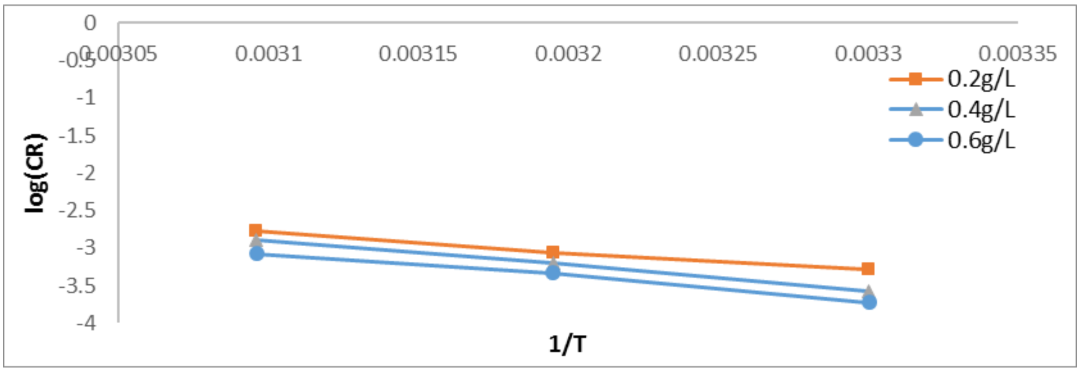


Fig.4. Arrhenius plot for the variation of plant extract concentration on the corrosion of mild steel in 0.9M HCl

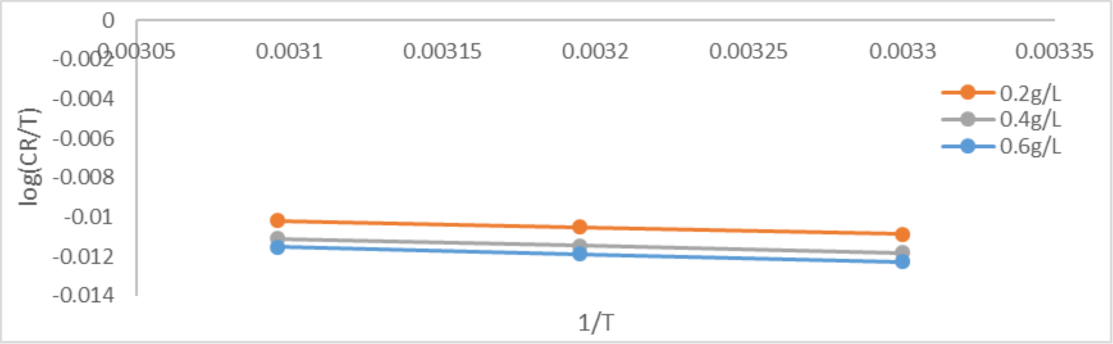


Fig.5. Eyring plot for the variation of plant extract concentration on the corrosion of mild steel in 0.9M HCl

3. EXPERIMENTAL

The leaves sample of the *Sarcocephalus latifolius* plant were collected in the Nigerian state of Benue's Akpuuna village, which is close to Kyado in the Mbaterem Ukum local government area. The leaves sample was then taken to the laboratory for pretreatment. The sample of leaves was cleaned with distilled water, allowed to dry at room temperature, then was sliced into smaller pieces. 500g of the chopped *Sarcocephalus latifolius* particles sample was weighed and immersed in 2.5L of methanol for 2 weeks, stirring continuously at regular intervals. The extract was filtered using Whatmann No 1 filter paper after percolation. After removing superfluous methanol, the extract was concentrated using a rotatory evaporator. To achieve a consistent mass, the sample was held at room temperature. The sample was kept in an ambient temperature until a constant mass was obtained. The sample was kept in the desiccator to avoid been contaminated.

3.1 Preparation of Inhibitor Solution in 0.9M HCl

Relation given in equation 12 was used to prepare concentration of 0.9M HCl that was used for the preparation of 0.2 - 0.6g/L concentrations of *Sarcocephalus latifolius* methanol extract.

$$V_{stock}\,(ml) = \frac{M \times C \times V}{10 \times \%purity \times density} \qquad (12)$$

The extract's 0.2g, 0.4g, and 0.6g were measured out, dissolved in a 1000cm^3 solution of 0.9M HCl, and then utilized as the inhibited extract solutions. The extract was not present in the blank solution, which was used as a control. Where % purity and density are both characteristics of the corrodent, and M is the molar mass of the corrodent (HCl), C is the concentration of the HCl used (0.9M), and V is the final volume (HCl).

3.2 Preparation of the Mild Steel Coupons

To give the coupons a shiny surface, the mild steel was physically cut into dimensions of 4.0 cm 3.0 cm x 0.15 cm. The mild steel was then polished with silicon carbide abrasive paper (of grades #400 and #1000). The coupons were dried in acetone after being rinsed with distilled water. The mild steel sample's composition, as determined by the XRD elemental analysis, was Fe (81.37%), Na (9.3%), Al (5.76%), Zn (2.48%), Si (0.4%), Mn (0.27%), Nd (0.16%), Cr (0.08%), and Ti (0.07%), with the remaining carbon content demonstrating that the metal is manufactured steel.

3.3 Weight Loss Experiments

To calculate the weight loss of the tested coupons, the prepared mild steel coupons were submerged in the corrodent solution of 0.9MHCl with and without the plant extract for a duration of 1 hour, then removed, cleaned, dried in acetone, reweighed, and submerged once again for a total of 4 hours. Weight was measured and recorded before and after each immersion as well as after the full (4-hour) experiment [7]. The mild steel coupons were tested under total immersion circumstances in 100mL of a 0.2g/L–0.6g/L solution at temperatures of 303, 313 and 333 K, respectively. The difference between the weight of the coupons at a given period and their initial weight was assumed to be the weight reduction. The average results from each experiment were utilized in the subsequent calculations, which were conducted in triplicate for each test [9]. Equations 13-15 were used to compute the weight loss (Δw), corrosion rate ($gh^{-1}cm^{2}$), inhibition efficiency, and degree of surface covering (θ) from the beginning and final weights of the tested mild steel coupon.

$$\%IE = \left(1 - \frac{W_1}{W_2}\right) \times 100 \qquad (13)$$

$$\theta = 1 - \frac{W_1}{W_2} \qquad (14)$$

$$CR\ (g/hcm^{-2}) = \frac{\Delta w}{At} \qquad (15)$$

According to the expression, w_1 and w_2 represent the weight losses for mild steel in the presence and absence of *Sarcocephalus latifolius* extract, respectively; θ stands for the inhibitor's degree of surface coverage; A represents the metal coupon's area (in cm^2); t stands for the corrosion's time in hours; and Δw represents the weight loss (w_2 - w_1) of the mild steel coupon following the period, t [11–16].

3.4 Fourier Transform Infrared (FT-IR) Analysis

A mild steel degreased coupon measuring 3.0 cm by 4.0 cm was immersed differently in inhibited and uninhibited 0.9 M HCl solutions over a duration of 24 hours at room temperature. This was done to gain access to potential alterations in the functional groups of the plant extract caused by its interaction with the mild steel surface. As a control, dried extract of *Sarcocephalus latifolius* was used. The materials' absorption bands were measured using an Agilent Technology Cary 630 Fourier Transform Infrared Spectrophotometer. The sample was scanned 32 times at a resolution of $8cm^{-1}$ over a wave number range of 650 to 4000 cm^{-1} for the analysis [9-11].

3.5 Scanning Electron Microscopy (SEM) Analysis

The mild steel coupons were dipped in an inhibited solution for a 24-hour period at room temperature in order to prepare the surface morphology of both inhibited and uninhibited coupons with various extracts. The surface morphologies of the samples were examined using a PROX scanning electron microscope (Phenom World Eindhoven). A very little amount of the materials to be viewed spread on the stub materials and were then observed in the instrument to obtain micrographs at an accelerating voltage of 15.00kV and x1000 magnification [9]. A thin layer adhesive functioning as carbon glue was bonded to the stub.

4. CONCLUSION

Three different concentrations of *Sarcocephalus latifolius* methanol extract was used to inhibit mild steel coupons in 0.9M HCl solution at a temperature range of 303K- 323K. Surface characterization methods including SEM and FT-IR employed confirmed the adsorption of the plant extract onto the surface of mild steel metal at the studied conditions. Through weight loss experiments, it was established that the inhibition efficiency of the plant extract increases with an increase in its concentration and decrease in temperature. Thermodynamic parameters for the corrosion and inhibition process described the process to be feasible and spontaneous. The process of the inhibition was also established to follow first order kinetics with half-life values increasing with an increase in plant extract concentration. Values of activation energy and isotherm parameters derived showed that the process obey the mechanism of physical adsorption. These derived parameters for the inhibition process showed that the plant extract of *Sarcocephalus latifolius* used can be qualified to be a good corrosion inhibitor on mild steel surface in acidic media.

5. ACKNOWLEDGEMENTS

The authors wish to acknowledge the staff of Central Laboratory Complex, Bayero Unibersity, Kano, Nigeria for conducting the surface characterization analysis of the mild steel coupons.

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