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Corrosion inhibition potential of the methanolic crude extract of *Mimosa pudica* leaves for mild steel in 1 M hydrochloric acid solution by weight loss method

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ABSTRACT

The corrosion inhibitory activity of mild steel in 1M hydrochloric acid solution by *Mimosa pudica* leaves extract was examined by the weight loss method. The result reveals that the leaves extract performs well as a good eco-inhibitor of the corrosive action of HCl on mild steel. Inhibition efficiency obtained for the extract rises with higher concentration and exposure time but falls with increasing temperature. The mechanism of the adsorption mode of the extract’s molecules fits well with Langmuir adsorption isotherm which suggests that the phytochemical constituents, (tannins, saponins, flavonoids, alkaloids, phenols, and quinones) as qualitatively displayed by the preliminary screening, adsorb onto the metal surface by forming monolayer films. Kinetics study shows that the rate of metal corrosion in the acidic medium is a first-order reaction that is concentration-dependent.

Keywords: *Mimosa pudica, corrosion inhibition, crude extract, weight loss*

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INTRODUCTION

Plants are rich in readily available phytochemicals, where some are toxic and others are non-toxic; and have found their use for industrial applications. The part of the plant, be it a leaf, stem, bark and so on which are rich in natural chemicals that can be used as corrosion inhibitors [1]. Roots, seeds, leaves, stem, flower, or fruit extracts can serve as an inhibitor against corrosion in different ferrous and non-ferrous materials in diverse acidic media [2]. Plants are identified as natural sources of compounds with multifarious molecular structures and diverse in physical, chemical, and biological features [3,4]. Extracts from plants are utilized for traditional relevance including therapeutics and biofuels [5]. Naturally occurring molecules are used because they are cost-effective, highly abundant, and of environmental acceptance. As a result of these merits, plant extracts have gained consideration as corrosion inhibitors for certain metals and their alloys under different conditions [6,7]. These characteristics have made plants have great attention for consideration as the vital origin of eco-friendly corrosion inhibitors.

Metals remain a popularly used set of materials, especially in mechanical engineering and transport industries. They also find their use in electronics as well as building industries. Nevertheless, corrosion forms a big problem confronting the application of metals and alloys. The fundamental call for concerns about corrosion lies in safety, economics, and preservation. This gulp uploads of money in an attempt to substitute corroded structures, machinery, and compartments [8]. Steel has found its way in today's world of materials engineering. It is an essential part of buildings, offshore construction tools, transportation of pipelines, ranging from automobiles machinery, and weapons of war. Due to the weak corrosion resistance of steel, carbon steel, in particular, they are not suitable for use in an environment prone to corrosion except protectives are incorporated [9]. Due to the damages caused by corrosion to lives and properties including the economy of any affected country, researchers around the world have been working assiduously to provide various solutions to the problems of corrosion and these led to the production of inhibitors from a choice of sources either synthetic or natural.

Corrosion is simply a natural process accompanied by the gradual diminishing of metal surfaces due to reactions with environmental conditions like water and air. The resultant effect can be as much as injury or loss of human lives and collateral smash up. In the industries, corrosion damages metals, and alloy structures leading to an economic effect like repair, loss of products, and different kinds of pollution [10]. Corrosion of metals can be curtailed by putting chemical compounds on their surfaces. There are various means of curtailing corrosion and its spreading rate with a focus on improving the durability of the material [7]. One of the embarrassing practices for preventing or reducing corrosion is the use of inhibitors on metallic surfaces in contact with corrosion initiating environments. A corrosion inhibitor is any substance that reduces the rate of corrosion of an exposed metal surface on the addition of a suitable concentration to the metal [7].

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Corrosion inhibitors are being classified based on their mechanism of actions. One class is those which form a protective film of oxide via an oxidizing process while the other class is those which adsorb selectively on a metal surface and create a blockage against corrosive agents. Some organic-based materials have received attention to examine their corrosion inhibition activity [11]. To a large extent, studies have shown that virtually all organic compounds that possess heteroatoms show prominent inhibitory efficiency [12]. Notwithstanding the potential of the findings, some of these compounds are so expensive, toxic, and non-biodegradable breeding up pollution [13]. This brings the need to search for alternatives.

Mimosa pudica is a stout straggling prostrate shrubby plant with compound leaves sensitive to touch. It has spinous stipules and globose pinkish flower heads and grows as a weed in almost all parts of the country [14]. *Mimosa pudica* is a readily available plant that contains phytochemical constituents which makes it a potential corrosion inhibitor. This study aims at investigating the phytochemical constituents and green corrosion inhibition efficiency of the crude extract of *Mimosa pudica* leaf on mild steel in 1M HCl solution. Also, the kinetics, thermodynamics, and the mechanism of the reaction involved in the corrosion inhibition will be considered. *Mimosa pudica* is a readily available plant that contains phytochemical constituents which makes it a potential corrosion inhibitor.

EXPERIMENTAL

Preparation of the specimen

ASTM A36 carbon steel of weight % composition C: 0.28, Mn: 1.03, Cu: 0.20, P: 0.04, Si: 0.28, S: 0.05 and the remaining is Fe. The steel used for this study was cut mechanically into coupons of dimensions 2.0 cm × 1.8 cm × 0.2 cm. These coupons were manually polished with a hand file and then with silicon carbide papers of different grades, rinsed with ethanol and distilled water, degreased in acetone, dried, and kept in a desiccator before the studies. The corrosive environment (1 M HCl) was prepared by the dilution of analytical grade 37 % hydrochloric acid with distilled water.

Preparation of Mimosa pudica leaf extract

Mimosa pudica leaves were collected in Wesley University, Ondo State, Nigeria, thoroughly rinsed under running tap and shade-dried at room temperature for 4 weeks, and pulverized into a fine powder with an electric blender. 180 g of the powdered *Mimosa pudica* leaves were exhaustively extracted by maceration in 500 mL methanol for three days with occasional shaking and double-filtered with Whatman filter paper. The filtrate obtained was concentrated under reduced pressure with a rotary evaporator and allowed to be dry completely at room temperature

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in a fume cupboard. The powder extract obtained was dissolved in 1 moldm^{-3} HCl solution to acquire different concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 g L^{-1}.

Phytochemicals screening

The crude methanolic extract of *Mimosa pudica* was screened to check for secondary metabolites such as tannins, saponins, alkaloids, flavonoids, sterols, phenols, quinones, and anthraquinones. All of the reagents used for screening are of analytical grade [15].

Weight loss Measurement

Already weighed mild steel coupons were dipped into test solutions of 1 M HCl in the absence and presence of the various concentrations of plant extract for 3 hours at a temperature of 298, 308, 318, and 328 K. The coupons were retrieved, washed, dried and re-weighed. The weight difference of the coupons before and after immersion in the test solutions was calculated and expressed as weight loss. All tests were conducted in duplicates and the weight loss averages were used for calculations. The effect of time on the corrosion rate was examined for 15 hours using the same procedure as above with each coupon retrieved at 3 hours intervals. Using the weight loss information, the corrosion rate (C_R), inhibition efficiency (I.E.), and the surface coverage (θ) of the extract at different concentrations were evaluated using the equations below respectively [16-18].

$$C_R = \frac{\Delta w}{At} \quad (1)$$

Where; C_R is the corrosion rate, Δw is the weight loss in g (gram), A is the area of the coupon measured in cm^2 and t is the time in an hour.

$$IE = \frac{C_{R(blank)} - C_{R(inh)}}{C_{R(blank)}} \times 100 \quad (2)$$

$$\theta = \frac{C_{R(blank)} - C_{R(inh)}}{C_{R(blank)}} \quad (3)$$

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RESULTS AND DISCUSSION

Phytochemical Screening

Natural products are the richest of heterocyclic compounds having higher electron density [19]. The methanolic extract of *Mimosa pudica* leaves was preliminarily screened for phytochemical constituents qualitatively as presented in Table 1. The results showed the presence of saponins, tannins, flavonoids, phenols, quinones, and alkaloids while anthraquinones and sterols were absent. Previous studies have shown that chemical structures of most phytochemicals contain electron-rich bonds or heteroatoms which enhance their electropositivity [20]. The results are found to be in agreement with the previous published works which reported the presence of tannins, phenolics, flavonoids, saponins, steroids, fixed oils, amino acids, alkaloids [21,22]. Therefore, the inhibition efficiency of methanolic extract of *Mimosa pudica* leaves on mild steel can be linked to the phytochemicals in the extract. Corrosion inhibition of mild steel is made possible majorly by filling the unfilled d-orbitals with hetero-atoms.

The presence of phytochemicals such as tannin, phenols, and flavonoid insignificant amount makes green inhibitors a potential substitutes for the more costly and toxic traditional inorganic and synthetic corrosion inhibitors as they have electron-donating heteroatoms such as N, O, and S in abundance, in their aromatic or long carbon chain [23]. Eddy and colleagues [20] also reported that saponins, tannins, and alkaloids are active constituents of most green inhibitors, therefore the potency of *Mimosa pudica* leaves as corrosion inhibition can be associated with these active constituents. Generally, the inhibition activity takes place either by physiosorption i.e moving charges situated on the inhibitor molecules onto the metal surface, or chemisorption i.e. movement of electrons from molecules of the inhibitor to available d-orbital of the metal. These processes are enhanced as a result of π-electrons coupled with appropriate functional groups in the inhibitor [24].

Table 1: Phytochemical constituents of *Mimosa pudica* leaves extract

s/n	Constituents	Test/Reagent	Methanolic Extract
1	Tannins	Ferric chloride test	+
2	Saponins	Foam test	+
3	Flavonoids	NaOH test	+
4	Alkaloids	Dragendorff's reagent	+
5	Sterols	Liebermann-Burchard test	-
6	Phenols	Ferric chloride	+
		Liebermann's test	+
7	Quinones	Conc. HCl test	+
8	Anthraquinones	Borntrager’s test	-

+ : Present; **-** : Not Present

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Effect of concentration

Figure 1 and Table 2 presents the impact of the rate of corrosion of mild steel in 1M hydrochloric acid solution in different concentration extracts of *Mimosa pudica* leaves. It can be inferred that inhibitor concentration is an indicator of the rate of inhibition. This is because the rate of corrosion of the mild steel in acid decreases as the concentration of the extracts increases [25]. The values of weight loss reduce with increasing extract concentration. This reflects an increase in the spread of the adsorbed extract molecules, thereby forming a film-like barrier separating the surface of the metal from the acidic solution thereby limiting the corrosive effect. [26]. Therefore, we can infer that the *Mimosa pudica* leaves extract is effective in reducing corrosion of mild steel in acidic solution.

Figure 2 is a plot that shows that the inhibitory efficiency increases as the concentration of the extract increases; ranging from 0.2 g L^{-1} to 1.0 g L^{-1}. This increase arises from an increasing amount of molecules of *Mimosa pudica* leaf extract which is adsorbed on the metal surfaces due to increasing concentration [27]. This ensures the protection of the active sites by molecules of the inhibitor. The presence of more inhibitors on the metal surface leads to the emergence of a thin layer or layers that inhibit corrosion [28] Similar observations were observed and reported by previous investigators [29, 30].

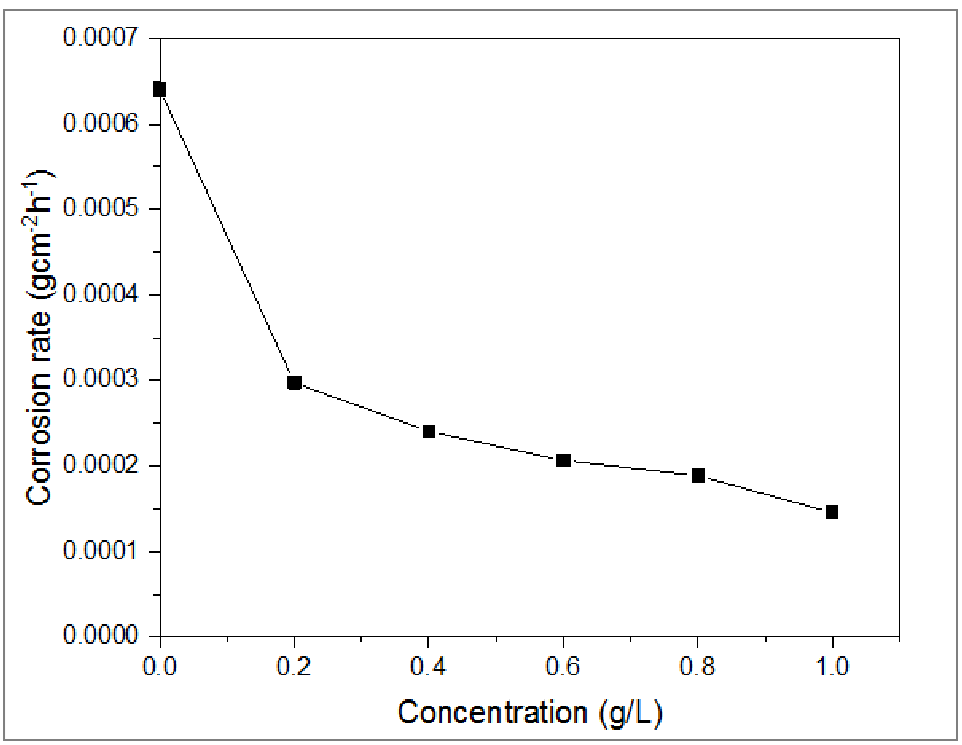

Figure 1: Effect of concentration of *Mimosa pudica* leaves extract on the corrosion rate of mild steel in 1 M HCl at 298K.

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Table 2: Surface Coverage (θ) and Inhibition Efficiency (%) for mild steel in 1M HCl solutions containing *Mimosa pudica* at 25 ^{0}C

Concentration [gL^{-1}]	Corrosion rate [$ghr^{-1}cm^{-2}$]	Inhibition efficiency [%]	Surface coverage [θ]
Blank	0.000642	-	-
0.2	0.000299	53.5	0.53
0.4	0.000243	62.2	0.62
0.6	0.000208	67.6	0.67
0.8	0.000191	70.3	0.70
1.0	0.000146	77.30	0.77

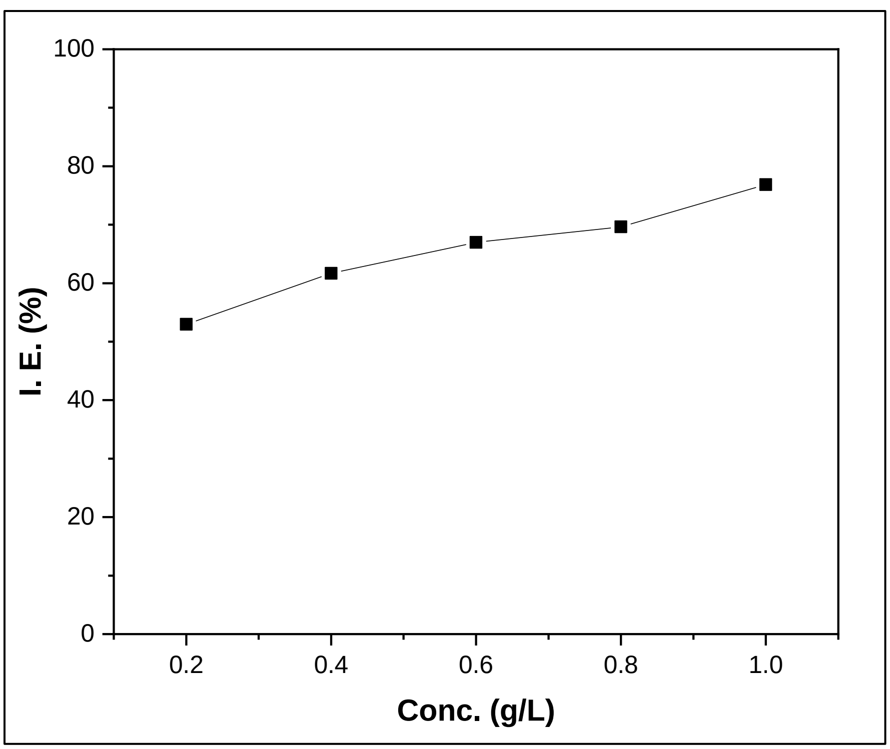

Figure 2: Effect of concentration of *Mimosa pudica* leaves extract on the inhibition the efficiency of mild steel in 1 M HCl at 298 K.

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Effect of Temperature

To measure how temperature affects corrosion rate in mild steel, we performed the weight loss experiment using temperatures ranging from 298 to 328 K at 10 K intervals in 1M HCl solution containing various concentrations of *Mimosa pudica* extract. This is to determine how stable the extract adsorbed layers on the mild steel surface [31]. The result shows that the corrosion rate increases with increasing temperature but reduces with increasing concentration of the extract (Figure 3). The increase in the rate of corrosion as a result of the temperature rise can be associated with an increase in the average kinetic energy of the reacting components, as the temperature is directly proportional to kinetic energy. However, a decrease in the corrosion rate arising from increasing extract concentration has to do with the inhibitory effect of the plant extract on mild steel. This is in line with the work of Olasehinde and colleagues [26] in 2016.

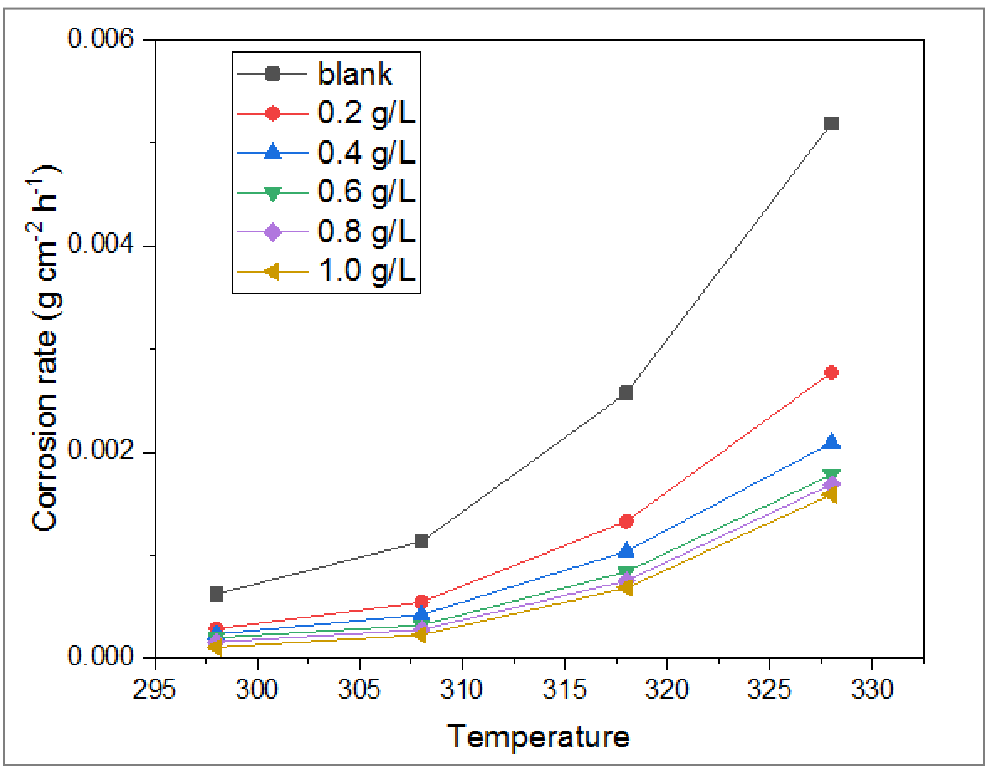

Figure 3: Effect of temperature on the corrosion rate of mild steel in 1 M HCl

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Also, the inhibition efficiency falls with rise in temperature (Figure 4). This shows that temperature has strong influence on how stable the extract film adsorbed on mild steel is in acidic solution [32]. The reduction in inhibitory efficiency with increasing temperature is described as indicative of the physical adsorption mechanism [33]. The Arrhenius equation was used to evaluate the activation energy of corrosion both in the presence and absence of inhibitor [34-36].

$$\ln C_R = -\frac{E_a}{RT} + \ln A \quad (4)$$

C_R stands for corrosion rate, E_a is for activation energy, R is for molar gas constant, T is for temperature (measured in Kelvin) and A is for Arrhenius pre-exponential factor.

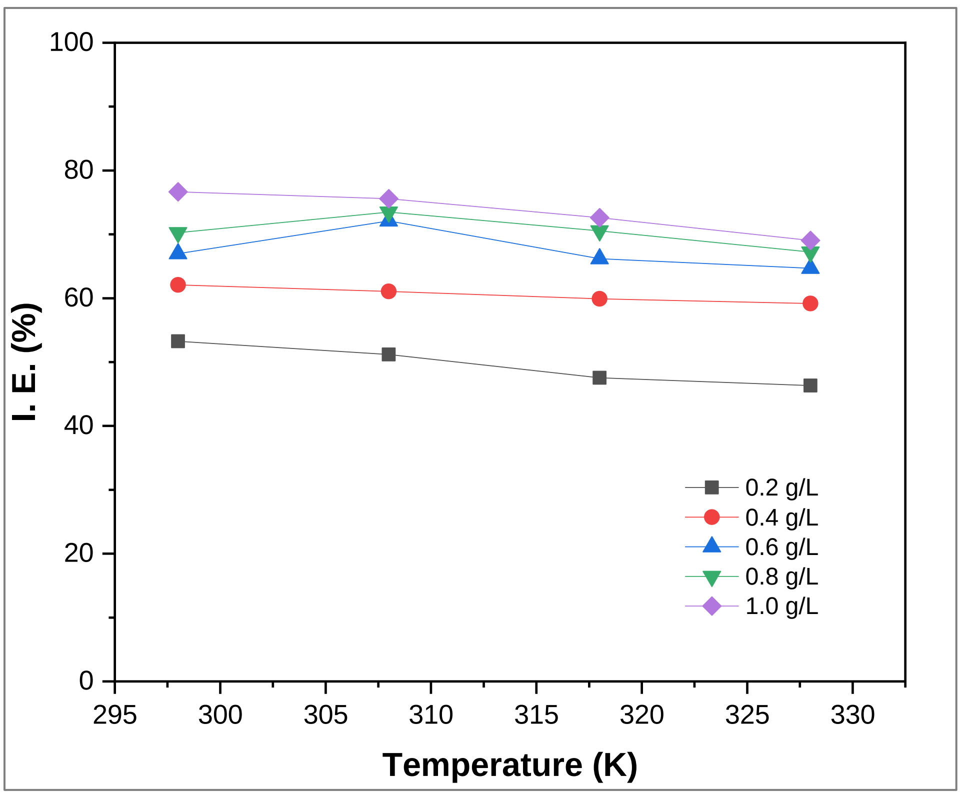

Figure 4: Inhibition efficiency of *Mimosa pudica* leaves extract on mild steel in 1 M HCl at various temperatures

Figure 5 demonstrates the plot of ln C_R against 1/RT while the values of the apparent energy of activation were determined from the slope of the graphs as presented in Table 3. It is observed that Ea rises with a rise in the concentration of the *Mimosa pudica* leaves extract. It has been

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reported that decrease in values of the activation energies in the presence of inhibitor as observed in this study might due to the chemical adsorption mechanism while the increasing Ea in the presence of inhibitor suggests a physiosorption mechanism [37,38]. Equation (5) was employed to determine relevant thermodynamic parameters such as a change in enthalpy (ΔH) and entropy (ΔS).

$$\ln\left(\frac{C_R}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

h stands for Planck constant, N stands for Avogadro's number, T for temperature (in Kelvin), R is for molar gas constant, ΔS is for the entropy of activation and ΔH stands for activation energy.

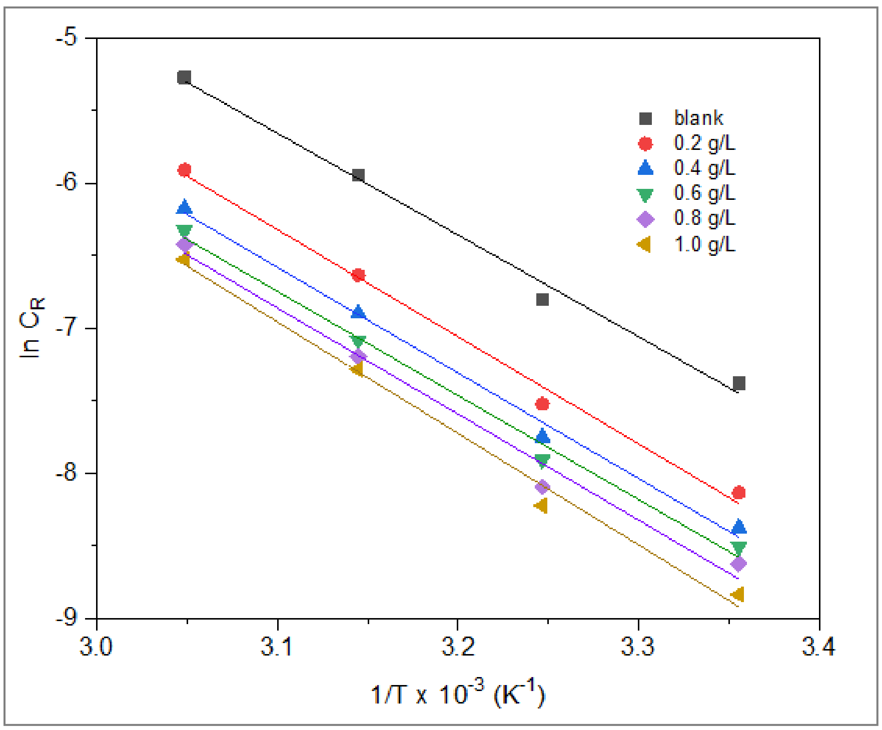

Figure 5: Arrhenius plots of lnC_R versus 1/T in the absence and presence of different concentrations of *Mimosa pudica* leaves extract in 1 M HCl

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Table 3: Thermodynamic parameters (entropy, enthalpy and activation energy) for mild steel dissolution process in 1 M HCl in the absence and presence of *Mimosa pudica* leaves extract

Concentration [g L^{-1}]	**ΔS [J mol^{-1} K]**	**ΔH [kJ mol^{-1}]**	**E_a [kJ mol^{-1}]**
Blank	-65.8	-6.93	57.6
0.2	-59.8	-7.37	61.3
0.4	-66.1	-7.21	59.9
0.6	-66.0	-7.28	60.5
0.8	-66.1	-7.30	60.7
1.0	-53.0	-7.83	65.1

A plot of log C_R/T against 1/T (Figure 6) produced a straight-line plot with a slope of (-ΔH/RT) and an intercept [ln(R/Nh) + (ΔS/R)]. Table 3 shows that the enthalpy of activation is negative for each extract concentration. The negative signs of ΔH reflecting the exothermic nature of the process of steel dissolution. The negative entropy values indicate that the activated complex is the slowest step of the reaction, which stands for a bond formation rather than bond breaking [39,40]. The negative values of entropy show decreasing disorderliness from the reactants to the activated complex [41]. Moreover, it establishes that the adsorption process is associated with lowering the entropy, that is a high chaotic degree before adsorption and then a reduced orderliness when the inhibitor gets adsorbed onto the mild steel surface [41].

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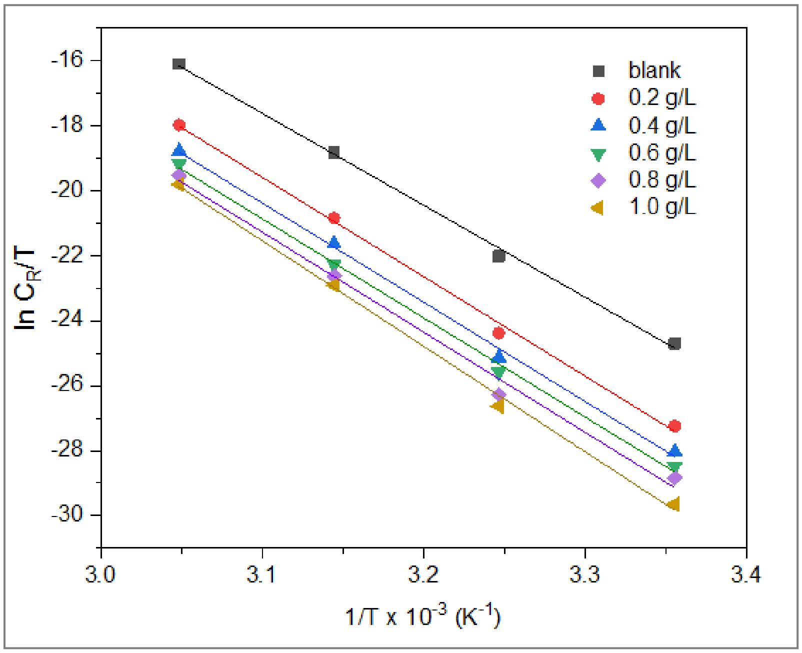

Figure 6: Eyring transition state plot for mild steel in 1 M HCl in the absence (blank) and presence of the methanolic extract of *Mimosa pudica* leaves

Effect of Time

The stability of the inhibitive behavior of methanolic extract of *Mimosa pudica* on mild steel with respect to time was investigated in 1M HCl acid solution. This was done both in the absence and presence of different extract concentrations at 3 hours interval at 298 K. The result shows that, although there was an increase in weight loss as time progressed, there was also a significant reduction as the extract concentration increases. The data obtained for the relationship between change in weight loss and time and various extract concentration fitted into equation 6 below. This helps to evaluate the rate of corrosion reaction in the presence of *Mimosa pudica* leaves extract.

$$\ln(w_i - \Delta w) = -kt + \ln w_i \tag{6}$$

w_i is the initial weight of the metal before immersion, Δw is the weight change, t is the immersion time and k is the rate constant [39]. The plot of $\ln(w_i - \Delta w)$ versus time (in days) demonstrate a linear relationship that confirmed a first-order reaction.

Figure 7 is a linear plot of $\ln(w_i - \Delta w)$ against time showing the adsorption of *Mimosa pudica* leaves extract on mild steel in 1 M HCl with R^2 values ≥0.98. The plots for all extract

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concentrations are all linear but showed a decrease trend in the values of ln (w_i - Δw) as the number of hours increases. The half-lives ($t_{1/2}$) of the corrosion were determined by using equation 7.

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

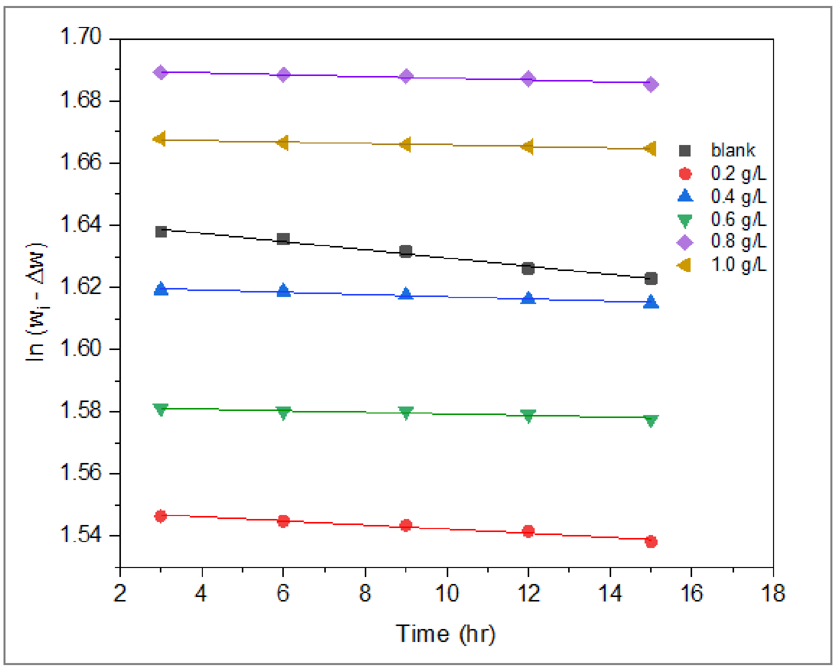

Figure 7: A plot of In(w1 – Δw) against Time for the adsorption of methanolic extract of *Mimosa pudica* leaves on mild steel at room temperature

It showed that the data points are well fitted into the first-order kinetics reaction. The rate constants of the mild steel corrosion at different concentrations of the extract were obtained from the slope of the graph, while the half-lives were calculated from the rate constant (Table 4). From the result obtained, we can infer that the rate constant of corrosion on the mild steel decreases as the extract concentration increases and the half-life of the reaction increases, where both remained steady at higher concentrations. This suggests that inhibition efficiency rises as the extract concentration rises, causing a decrease in the dissolution rate of the mild steel in 1M HCl. This is an indication of the further protective action of the *Mimosa pudica* leaves extract on the metal surface. These outcomes align with findings reported by Okafor, Olasehinde, and their co-workers [42,43].

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Table 4. Kinetic data for mild steel corrosion in 1 M HCl in the absence and presence methanolic extract of *Mimosa pudica* leaves extract.

Concentration [gL^{-1}]	**Rate constant, k [hr^{-1}]**	**Half-life, $t_{1/2}$ [days]**
Blank	0.0013	22.2
0.2	0.0007	41.2
0.4	0.0004	72.2
0.6	0.0003	96.2
0.8	0.0003	96.2
1.0	0.0003	96.2

Adsorption Isotherm

Organic molecules are the major effective inhibition constituents of the plants. Their corrosion inhibition mechanism is usually described based on molecular adsorption [32,38]. Adsorption isotherms help to illustrate the interaction between the inhibitor molecules and active sites of the metal surface [41,44]. The adsorption isotherm is crucial in understanding the mechanism of the heterogeneity of organic and electrochemical reactions [45]. The results of the present study fit Langmuir, Freundlich, and Temkin isotherms but the Langmuir isotherm gives the best fit with very strong correlation coefficients (R^2) for different *Mimosa pudica* extract concentration in 1M HCl at various temperature. Langmuir adsorption isotherm is represented in equation 8 below:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{8}$$

C is the extract concentration, K_{ads} stands for equilibrium constant of adsorption and θ represents the degree of surface coverage of the inhibitor.

As shown in Figure 8, plotting C versus C/θ results in a linear correlation wherein the value of C/θ rises as the extract concentration rises. The strong correlation ($R^2 = 0.99$) for all the extract concentrations and at different temperature implies that inhibition adsorption on mild steel agrees with the Langmuir isotherm. This denotes the adsorbing *Mimosa pudica* leaves extract occupy certain adsorption sites on the metal surface.

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The equilibrium constant of adsorption for *Mimosa pudica* extract on mild steel surface relates to Gibb's free energy of adsorption, ΔG, by

$$\Delta G_{ads} = -RT \ln (55.5\ K_{ads}) \tag{9}$$

R stands for molar gas constant, T represents absolute temperature, 55.5 indicates a molar concentration of water in the solution and K_{ads} represents adsorption constant.

Adsorption constant values increase as temperature increases. This shows that the interaction between the adsorbed molecules and the metal surface becomes strengthened where the molecules of the inhibitor possess strong interactions with a metal surface. These results show an increase in protection efficiency as the temperature increases. The values of ΔG_{ads} evaluated from the intercept of the plot of Langmuir adsorption isotherm reflect high adsorption capability. The negative Gibb's free energy (ΔG_{ads}) values shown in Table 5 indicate that the adsorption process is spontaneous and that the adsorption layer on the mild steel is very stable.

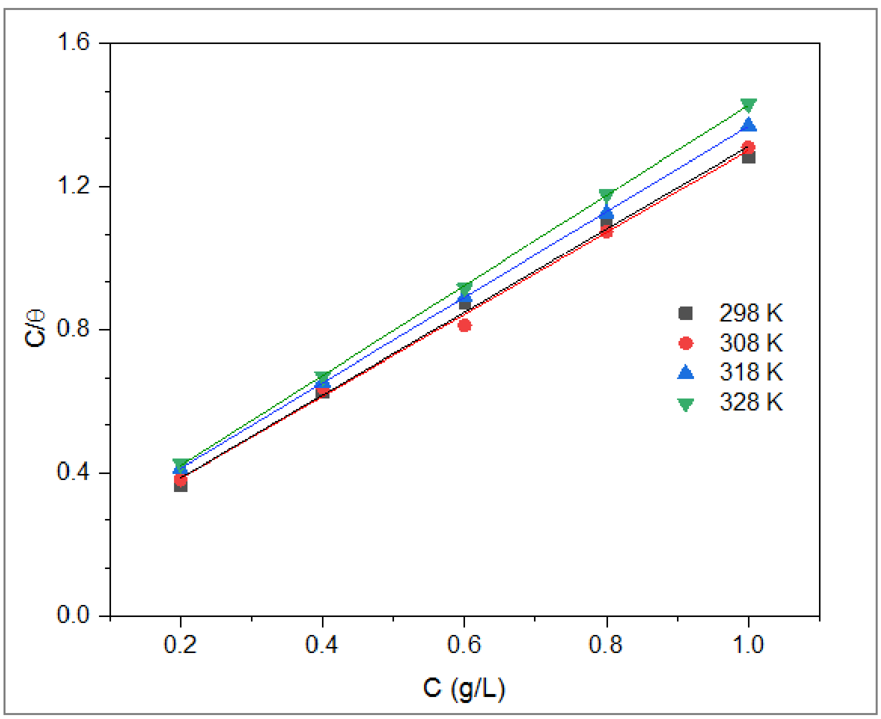

Figure 8: Langmuir adsorption isotherm plot for mild steel corrosion in 1 M HCl for the methanolic extract of *Mimosa pudica* leaves at different temperatures

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Table 5: Calculated parameters from Langmuir adsorption isotherm for *Mimosa pudica* leaves extract

Temperature [K]	K_{ads}	ΔG_{ads} [kJ/mol]	R^2
298	5.98	-14.4	0.99
308	6.04	-14.9	0.99
318	5.44	-15.1	0.99
328	5.95	-15.8	0.99

CONCLUSION

Mimosa pudica leaves extract has been shown by the present study to be a good inhibitor for the corrosion of ASTM A36 carbon steel in hydrochloric acid solution. The inhibition efficiency of the extract increased with concentration but decreased with temperature. The ability to protect the surface of the mild steel is associated with the presence of secondary metabolites such as alkaloids, flavonoids, saponins, quinones, tannins, and phenolic compounds which adsorb to the surface by physiosorption in a monolayer manner as confirmed by thermodynamic and Langmuir isotherm studies. The potential of *Mimosa pudica* leaves extract should be further explored in other corrosive environments like sulphuric and nitric acids since they are also employed in industries for oil-well acidization and pickling. Future research should also include isolation and structural elucidation of *Mimosa pudica* plant extract to shed more light on the corrosion inhibition process.

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