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Adsorption, Thermodynamic and Kinetic Studies of *Piliostigma thonningii* Leaves extract as Corrosion inhibitor on Mild Steel in 0.5 M H_2SO_4 Solution

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Abstract

The inhibitive effects of *Piliostigma thonningii* leaf extract on the corrosion of mild steel in 0.5 M H_2SO_4 solution have been investigated using weight loss measurements, kinetics, adsorption, and thermodynamic study. The results obtained showed that the corrosion effect of *Piliostigma thonningii* leaf extracts was found to be dependent on extract concentration, and the inhibition efficiency reached up to 97.84% at 0.5 g/L. Leaf extract adsorption on mild steel followed the Langmuir adsorption isotherm at all test temperatures, according to weight loss and adsorption experiments. The corrosion inhibition process was spontaneous, and molecules were adsorbed on the metal surface through both physical and chemical adsorption, according to thermodynamic characteristics obtained from temperature studies. Fourier transform infrared spectroscopy and scanning electron microscopy were used to describe the surface morphology of mild steel. The extract's inhibitory effect may result from its constituents adhering to mild steel. Additionally, kinetic examination of the inhibitory process shows that it adheres to the first-order kinetic model, with half-life values increasing as the plant extract concentration increases.

Keywords: *Adsorption, Kinetic, Thermodynamics, Corrosion*

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1.0 Introduction

The environment is becoming progressively corrosive to all materials, including metals and alloys. Air and water pollution, along with various industrial by-products including chlorine, ammonia, sulphur dioxide, and fuel gases, are significant contributors. Inorganic acids, including hydrochloric, sulphuric, and nitric acids, together with other deleterious substances such as steam, solvents, alkalis, and organic acids, exhibit corrosive properties (Douglass *et al.*, 2004; Bouklah *et al.*, 2004).

The most often used inorganic acid is sulphuric acid (H_2SO_4). As a result, sulphuric acid causes the most common corrosion in chemical processing. This inquiry focuses on the behaviour of mild steels in sulphuric acid, which presents a number of extremely complicated issues. In essence, the acid is neither very reducing nor very oxidizing. Depending on the oxidizing or reducing chemicals in the solution, mild steels can either be passivated or activated. Additionally, some contaminants may have an impact on a system's corrosion behaviour. These contaminants are found in both the produced acid and the materials that were treated with the acid. While some of these contaminants might slightly slow down the attack, others might speed it up. However, some contaminants may not affect how materials corrode, while others might significantly reduce the acid's corrosiveness (Adreani *et al.*, 2015).

Corrosion is the slow deterioration of materials due to their interaction with the environment. It is a significant industrial issue that has drawn many researchers in recent years. From an application perspective, corrosion management is crucial, and it has been noted that the usage of inhibitors—which function as a barrier to lessen the aggressiveness of the surroundings against the corrosion attack—is required (Shang *et al.*, 2010). Numerous organic heterocyclic compounds have been identified as corrosion inhibitors. It has been demonstrated that organic compounds with long carbon chains, aromatic ring systems with greater electron density, or heteroatoms like oxygen, nitrogen, sulfur, and phosphorus have the ability to inhibit corrosion (Ghazoui *et al.*, 2014; Siaka *et al.*, 2014; Al Aoufir *et al.*, 2016). Nevertheless, the majority of synthetic organic inhibitors are hazardous and pose different risks when released into different streams. our is a recent worry for the majority of chemical suppliers and operators, who must adhere to increasingly strict rules and regulations that minimize the impact of chemicals on aquatic life, humans, and other animals that share our universe. In the past, the application of various inorganic and organic inhibitors, including volatile inhibitors, passivating inhibitors, film inhibitors, and cathodic inhibitors, has been welcomed, especially in the oil and gas industry where they have produced favorable outcomes in terms of decreased installation failure and consequently increased revenue (Siaka *et al.*, 2014).

However, there are certain concerns regarding the stability and health implications of inorganic and organic inhibitors, despite their successes in controlling corrosion in all applications of metals, especially

during acid pickling action on well turbine, oxidizing process, tank descaling, and industrial cleaning. Due to their high level of toxicity, chromium compounds used to control metal corrosion in aquatic environments are prohibited in all industries (Taleb *et al.*, 2011).

Another inhibitor lanthanide salts, have been used until it was reported to be toxic and carcinogenic in nature. Furthermore, synthesized organic inhibitors have been proven to be useful in terms of their stability to dissolve completely in aqueous environment that is corrosive, their ability to easily get attracted to metal surfaces and the stability with them when they absorbed. This has led to the exploring and increase demand on using natural originating products which would have better chances of being eco-friendly and harmless (Nicholson *et al.*, 2010; Afia *et al.*, 2012).

The cost of implication of corrosion at global level is nothing different from that locally in Nigeria. With the continuous growth in the oil and gas industry massive capital expenditure continues. In addition, in response to the global need for fossil oil there has been improvement in technology and techniques to explore oil and gas in both onshore and offshore facilities. Report on the oil and gas enhanced Production Service Industry 2006, the increase in demand has also come with so much pressure on all facilities which in turn increase the cost of maintenance which has hit all time high mark, a research conducted ten years ago reveal that Europe's average major containment hazards recorded from 180 to 2006 were all associated with technical failures of plant facilities. These failures are expanded to include aging, erosion, and fatigue. Indeed, it can rightly be said that the western world has had its share of the devastating effect corrosion (Chahul *et al.*, 2019).

(National Association of Corrosion Engineer, NACE, (2016), recently put the annual cost of corrosion at a whooping estimate of $ 1.372 billion. When broken down this figure shows that $589 million was spent managing pipeline surfaces and facility. $463 and $320 million were spent annually managing corrosion related to down whole tubing and capex association with corrosion control respectively. The report also puts the cost of corrosion mitigation at US$2.5 trillion, about 3.4% of the world GDP. The staggering cost is calculated based on the estimate about 5000 kg of steel degenerate per second all over the world, 40% of all steel produce are used as replacement parts of part of the assets that have been corroded while, 60% of the offshore fleets all over the world have been use beyond their estimated 20 years design age. Another 6 tons of 60% of the offshore fleet all over the world have been used beyond their estimated 20 years design age (Guruprasad *et al.*, 2020).

2 Materials and methods

a. **Preparation of Mild Steel Specimens for Test**.

Mild steel sheet was purchase from iron sheet merchant at Kofar ruwa market Kano state, Nigeria and cut in to same size (2cm x2cm x 0.21cm**).** The mild steel sheets were separately polished mechanically

with silicon carbide emery papers and washed with deionized water, degrease with methanol, dried in acetone and kept in moisture free prior to each experiment carried out as made mentioned by (Nwoso *et al.*, 2020).

b. Collection, Identification, preparation, and Extraction of Plants Materials

Samples of *P. thonningii* leaves were obtained from new site Bayero University, Kano state, Nigeria on the 15th june, 2021 and the leaves were authenticated by Mr Habu of the Herbarium in the Department of plant Biology, Bayero University Kano, Nigeria where voucher specimen No 23 was deposited. The leaves were air dried under the shade for 14 days and then powdered using pestle and mortar and sieved through 75µm mesh and hence referred to as the powder plant material stored for use. The powdered plant material (800g), were soaked in a 1Litre solution of ethanol (95% purity) for 72 hours. After 72 hours, the sample is filtered and the filtrates obtained was further allowed to evaporate for a week in order to make it free of ethanol. The stock solutions of the extract were used to prepare different concentrations of the extract by dissolving 0.1, 0.2, 0.3, 0.4, 0.5g of the extract in 1Litre of deionized water for weight loss and electrochemical analyses (Nwoso *et al.*, 2020).

c. Preparation of the corrosive solution

The corrosive solution used in this study is 0.5 M sulphuric acid solution and was prepared using equation 1 below :

$$V_{stock}\,(ml) = \frac{M \times C \times V}{10 \times \%\, purity \times density} \qquad (1)$$

Where M is the molar mass of the acid, C is the final concentration of the acid (0.5 M), V is the final volume of the solution, V_{stock} is the volume of the concentrated acid before dilution.

d. Determination of physicochemical properties of *Piliostigma thonningii* leaf extract

Physicochemical parameters such as yield (%), PH, moisture content (%), and bulk density (g/ml) were determined using standard methods. The Fourier Transform spectroscopic analysis of the *Piliostigma thonningii* leaf extracts was also done (Columbier *et al.*, 2012).

e. Surface characterization

The surface of fresh, corroded and inhibited mild steel was analysed by using sophisticated scanning electron microscopy (SEM). Scanning electron microscopy (SEM) studies two cleaned mild steel specimens were immersed separately in 50ml of blank (uninhibited 0.5M sulphuric acid) and inhibited 0.5M sulphuric acid solution with 0.5g/L extract for 48 hours, after which the mild steel sheets were removed and dried in air. The dried mild steel sheets were then subjected to scanning electron

microscopy (SEM) for visual physical surface morphology of steel coupons inhibited with *Piliostigma thonningii* leaves extract (inhibitor) and uninhibited coupons (Eddy *et al*., 2008).

f. Measurement of corrosion effects using weight loss method

Each pre- weighed mild steel sheet was separately immersed in 50 ml each of different inhibitor leave extract concentrations (0.1, 0.2, 0.3, 0.4, and 0.5 g/L) and 50 ml of 0.5M H_2SO_4 solution without inhibitor (blank solution). The beakers were placed in a thermostated water bath. The experiment was conducted at various temperatures of 303, 313, 323, 333, and 343K for 3 hours each. Corrosion rate (CR) and percentage corrosion inhibition efficiency were calculated using the equations (1) and (2) as follows

$$CR\ (gcm^{-2}h^{-1}) = \frac{W}{At} \quad (2)$$

$$IE\ (\%) = \frac{(W1 - W2)}{W1} \times 100 \quad (3)$$

Where W, A and t are weight loss (mg), exposed area (cm^2) and minimum time (h) respectively while W_1 and W_2 indicate weight loss in by mild steel in either uninhibited solution (blank) or inhibited solution of leaves extract (Elouadi *et al.*, 2015).

3. Results and discussion

a. Physicochemical Analysis

Table 1. Physicochemical Properties of raw leaves and leaves extract

Physicochemical properties	Raw leaf	Leaf extract
Yield (%)	N.A	16.82
pH	5.4	4.8
Conductivity (U̍s/cm)	719.2	451.24
Moisture content	15.21	12.81
Bulk density (g/ml)	0.38	0.49

Where N.A = not applicable

From Table 2 the moisture content of extract of *piliostigma thonningii* was found to be 12.81% and bulk density is 0.49 g/ml while PH and conductivity were found to be 4.8 and 451.24. It could be observed that PH of raw leaf is comparable to its extract as both fell within acidic region of respectively. All values of various parameters of raw leaves were found to be higher than its corresponding extracts with exception of bulk density where the leaves extracts were found to be greater in value.

Table 2. Composition of mild steel

Element	% by weight
Fe	97.54
Mn	0.04
C	0.15
Ti	0.88
V	0.79
Al	0.01
Ni	0.01
Cr	0.03
Si	0.03

b. Weight Loss Measurement

Table 3 reports the weight loss experimental findings of *Piliostigma thonningii* leaves extract corrosion inhibition on mild steel in 0.5 M H_2SO_4. The findings are obtained by the following experimental conditions: temperature between 303 K to 343 K were varied in a series with a common difference of 10 K at various inhibitor concentrations of 0.1g/L, 0.2 g/L, 0.3 g/L, 0.4g/L, and 0.5 g/L in aqueous environment with 0.5 M H_2SO_4. The results obtained are given in table 3 in which the inhibition efficiency increases with increase in inhibitor concentration reaching 97.84% at 303 K. However, inhibition efficiency decreases with increase in temperature, in reaching the lowest value 88.86% at 343 K, indicating that *Piliostigma thonningii* leaves extract is stable at lower temperature.

c. Effect of temperature

The mean kinetic energy of the reactant species in any system is thermodynamically dependent on the temperature. Figure 2, illustrates the effect of temperature on the weight loss of mild steel in uninhibited and inhibited acid solutions. Figure 2 shows the general increase in corrosion rates of the steel coupons at higher temperatures. This was observed in both the uninhibited H_2SO_4 and on addition of leaves extract. Reacting species usually acquire more kinetic energy at higher temperatures; this explains the higher corrosion rates of the steel coupons in the test solution as temperature increased. Again, the presence of leaves extract in the inhibited test solution is seen to decrease the rate of corrosion of the mild steel coupons. Decrease in inhibition efficiency of the leaves extract with temperature at all the concentration investigated. This behaviour has reported to be due to the agitation of the adsorbed inhibitor and its consequent desorption from the surface of the mild steel at high temperatures, signifying physiosorption (Amitha *et al.*, 2011).

Table 3: Corrosion parameters of mild steel in 0.5 M H_2SO_4 in various concentration of leaves extract at different temperature using weight loss techniques.

LEC (g/l)	WL (g)	Temperature (K)	CR ($gcm^{-2}h^{-1}$)	Θ	IE (%)
Uninhibited	0.551	303K	0.0918	0.8935	N.A
0.1	0.249		0.0415	0.9514	95.14
0.2	0.213		0.0355	0.9527	95.27
0.3	0.191		0.0318	0.9582	95.82
0.4	0.117		0.0195	0.9754	97.54
0.5	0.103		0.0171	0.9784	97.84
Un-inhibited	0.794	313K	0.1323	0.8392	N.A
0.1	0.409		0.0682	0.9176	91.76
0.2	0.355		0.0592	0.9293	92.93
0.3	0.256		0.0427	0.9467	94.67
0.4	0.253		0.0421	0.9492	94.92
0.5	0.201		0.0335	0.9614	96.14
Un-inhibited	0.933	323K	0.1555	0.8206	N.A
0.1	0.496		0.0827	0.9005	90.05
0.2	0.415		0.0691	0.9164	91.64
0.3	0.329		0.0548	0.9351	93.51
0.4	0.309		0.0515	0.9373	93.73
0.5	0.257		0.0428	0.9474	94.74
Un-inhibited	0.981	333K	0.1635	0.8044	N.A
0.1	0.525		0.0875	0.8936	89.36
0.2	0.448		0.0746	0.9146	91.46
0.3	0.306		0.0510	0.9389	93.89
0.4	0.211		0.0351	0.9587	95.87
0.5	0.118		0.0196	0.9770	97.70
Un-inhibited	1.001	343K	0.1668	0.8075	N.A
0.1	0.555		0.0925	0.8886	88.86
0.2	0.491		0.0818	0.9012	90.12
0.3	0.355		0.0591	0.9288	92.88
0.4	0.261		0.0435	0.9484	94.84
0.5	0.205		0.0342	0.9581	95.81

LEC= leaves extracts concentration, WL = Weight loss, CR = Corrosion rate, Θ = Degree of surface coverage, IE = Inhibition efficiency, N.A = Not applicable

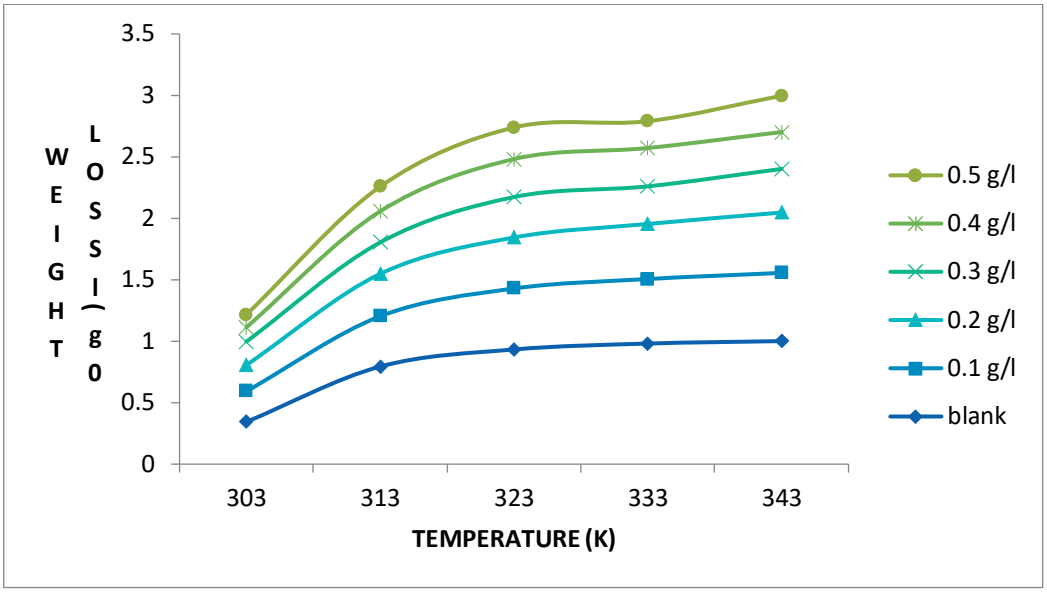


Figure 1 Effect of Temperature on corrosion rate of mild steel in 0.5 M H_2SO_4 inhibited with *piliostigma thonningii* leaves extracts solution at various temperature ranges (303K ─343K).

d. Effect inhibitor concentration

The value of the percentage inhibition efficiency IE (%) and corrosion rate (W) obtained from weight loss method at different concentrations of *piliostigma thonningii* leaves extract are summarized in Table 1. The result obtained in Table 3 indicated that the corrosion rate (W) of mild steel decreased continuously with increasing the inhibitor concentration, i.e. the corrosion of steel is retarded by *piliostigma thonningii* leaves extract.

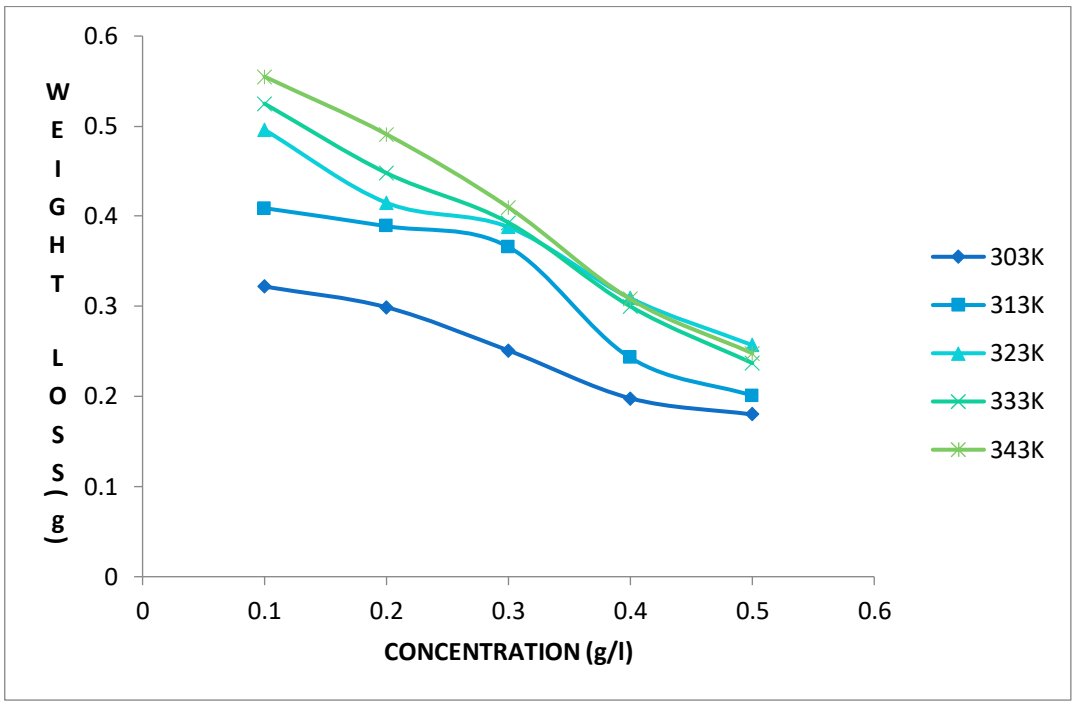


Figure 2. Concentration versus weight loss

However, the inhibition efficiency (Ew) increases sharply with increase in concentration of inhibitor reaching a maximum value of 97.88%. This behaviour could be explained by the adsorption of phytochemical components of the *piliostigma thonningii* onto the mild steel surface resulting in the blocking of the reaction sites, and protection of the mild steel surface from attack of the corrosion active ions in the acid medium (Gopal *et al*., 2015). We can conclude that the *piliostigma thonningii* is a good corrosion inhibitor for mild steel in different concentration of sulphuric acid.

e. Effect of immersion time

The effects of immersion time on corrosion rate (CR) and inhibition efficiency (IE) in 0.5 M sulphuric acid environment is shown in Table 4. The corrosion rate (CR) and inhibition efficiency (IE) were calculated using their respective formulas as at 2 hours interval for total of 12 h in an uninhibited 0.5 M H_2SO_4 and in the presence of maximum concentration of the leaves extracts at 298 K (Igwe *et al.*, 2018). The plot reveals the that the rates of corrosion of mild steel in the acidic medium generally increased with time leading to greater loss in weights, with blank giving the highest value of corrosion rate. From the table, it was observed that corrosion rate in uninhibited 0.5 M H_2SO_4 increased from 0.166 $g.cm^{-2}h^{-1}$ after 2 hours immersion to 0.459 $g.cm^{-2}h^{-1}$. after 12 hours of immersion time. This trend also occurred when inhibited with 0.5 M H_2SO_4 solution with leaves extract also followed the same trend. But the rate of corrosion increases was obtained to be greatly reduced from 0.332 $g.cm^{-2}$ h^{-1} after 2 hours of immersion time to 0.917 $g.cm^{-2}h^{-1}$ after 12 hours of immersion time and this could be attributed to the presence of leaves extract that inhibited the corrosion rate (Al-otaibi *et al*., 2014; Aourabi *et al*., 2014).

Table 4. Effects of Immersion time on Extent of Corrosion of Mild Steel in Uninhibited 0.5 M H_2SO_4 Solution and with 0.5g/l leaves Extract at 298 K.

Immersion Time (h)	WL (g) uninhibited	WL (g) Inhibited	CR($g/^{cm-2}h$) uninhibited	CR(g/cm) inhibited	Θ	I/E
2	0.332	0.036	0.166	0.018	0.9323	93.23
4	0.397	0.081	0.198	0.041	0.9150	91.50
6	0.661	0.131	0.331	0.066	0.8655	86.56
8	0.720	0.186	0.360	0.093	0.8624	86.24
10	0.789	0.197	0.395	0.094	0.8442	84.42
12	0.917	0.219	0.459	0.100	0.8093	80.93

WL means weight loss; CR is corrosion rate, Θ represents surface coverage and IE is inhibition efficiency.

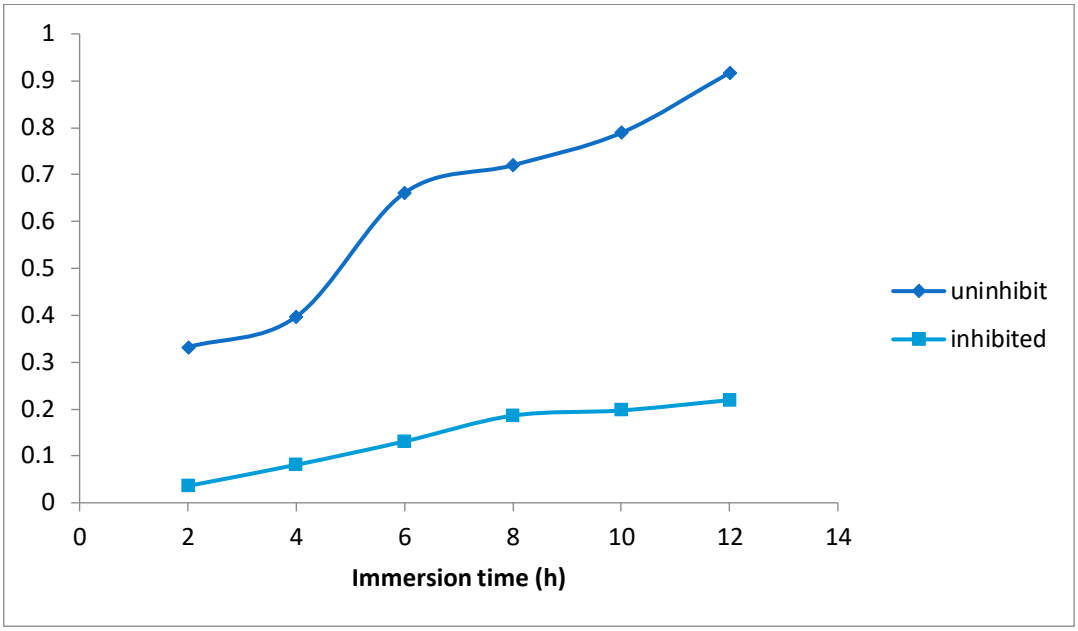
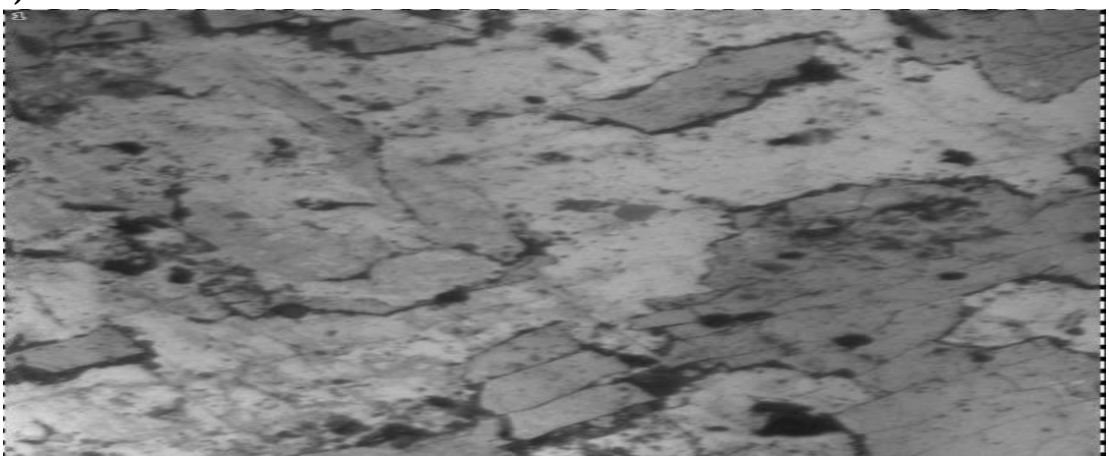


Figure 3. The effect of immersion time on corrosion rate of mild steel immersed in 0.5 M H_2SO_4 solution and inhibited with 0.5 g/l leaves extracts.

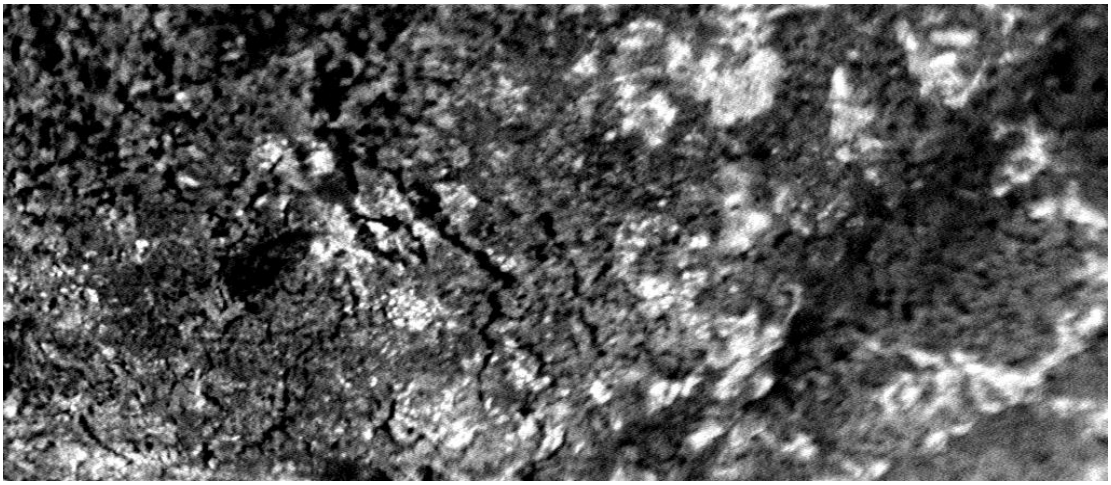
f. Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy analytical technique revealed the visual physical morphological changes on the surface of the mild steel that were separately immersed in unhibited 0.5 M H_2SO_4 solutions and in the inhibited H_2SO_4 containing 0.5 g/l of *piliostigma thonningii* leaves extract. SEM images for mild steel revealed that in the absence of inhibitor, rough and a lots of pits and cavities resulted from corrosion attack on the surface of mild steel in an uninhibited medium while the damages on corroded areas were reduced in the SEM images of the mild steel inhibited with optimum concentration of *piliostigma thonningii* leaves extract. This is due to the formation of protective layers by the molecules of the inhibitor inhibiting the corrosion of mild steel. SEM image of pre-treated mild steel revealed smooth surface because it was not exposed to corrosion agent (Aprael *et al.*, 2011).

(a)



(b)



g. Thermodynamic Study

Thermodynamic parameters are important to understand the inhibition mechanism. The thermodynamics functions for dissolution of mild steel without and with the addition of optimum concentration of *piliostigma thonningii* at various temperatures were calculated from logarithm of corrosion rate (CR) of metal in acid H_2SO_4 solution by using the Arrhenius equation:

$$CR = A exp^{-E_a/RT} \qquad \text{Arrhenius equation} \qquad (4)$$

$$\text{Log CR} = \log A - \frac{E_a}{2.303RT} \qquad (5)$$

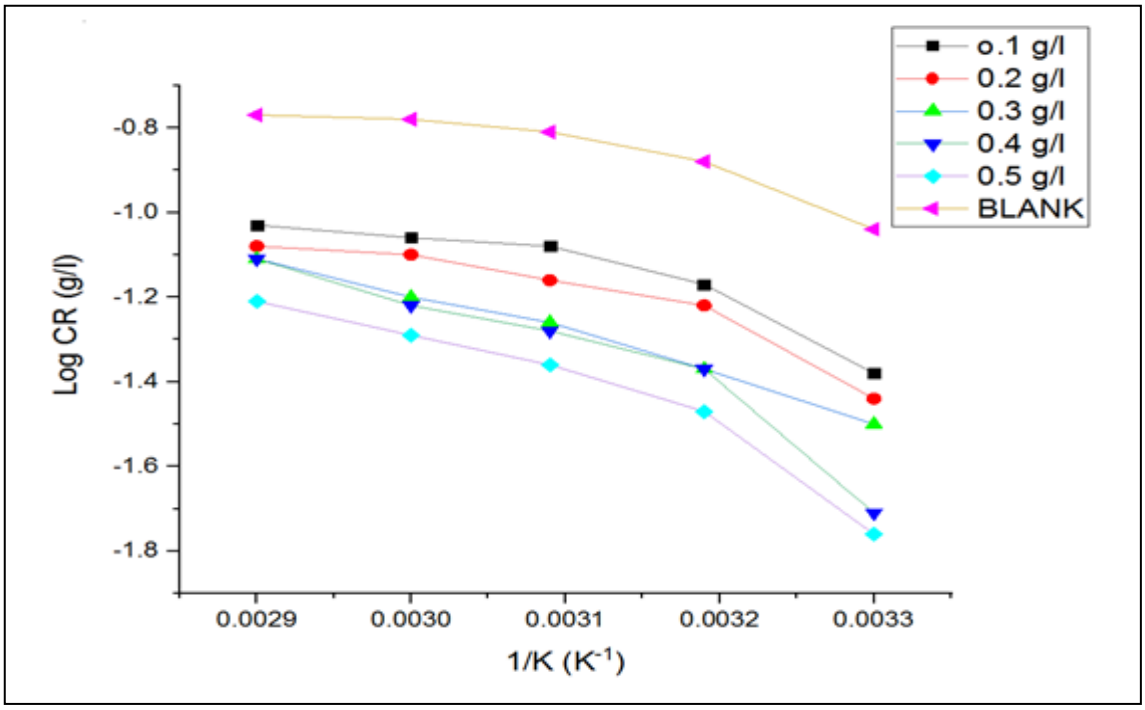


Figure 4 : Arrhenius plots for mild steel corrosion rates (W) in 0.5 M sulfuric acid in the presence of various concentration of *piliostigma thonningi*

In order to calculated activation parameters for the corrosion process, alternative formation of Arrhenius called transition state equation can be used:

$$\text{Log } {}^{CR}/_{T} = [\text{Log } ({}^{R}/_{nh}) + {}^{\Delta S^*}/_{2.303R}] - {}^{\Delta H^*}/_{2.303RT} \quad \text{Transition state equation} \quad (6)$$

CR is the corrosion rate,(ΔH), enthalpy of activation and (ΔS), is the entropy of activation, h is the Planck's constant (6.6261× 10^{-34}Js), n is Avogadro's constant 6.0225×10^{23} and R is the molar gas constant.

A plot of Log CR/T versus 1/T is a straight-line graph with slope ($\text{Log} - DH/2.303R$) and an intercept $[\text{Log } (R/nh) + DS/2.303R]$ from which DH, DS were calculated, Figures 4 & 5, Table8, (Bentiss *et al.*, 2022).

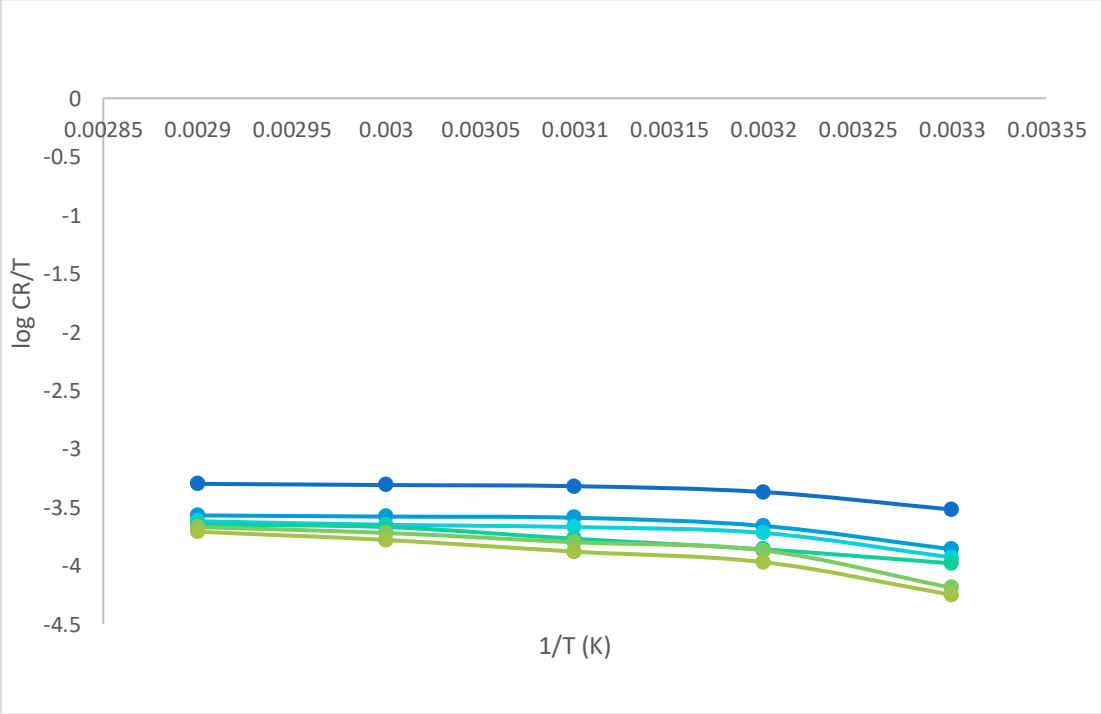


Figure 5 : Transition state plots for mild steel corrosion rates (W) in 0.5 M sulfuric acid in absence and presence of various concentration of *piliostigma thonningii* leaves extract

Table 8 Thermodynamic activation parameters

Concentration (g/L)	E_a (kJ/mol)	$\Delta H^{\times}$ (kJ/mol)	ΔS (kJ/mol)
Blank	5.32	4.15	-212
0.1g/l	6.73	5.48	-210.1
0.2g/l	6.82	5.73	-210.6
0.3g/l	7.89	7.06	-207.1
0.4g/l	11.47	8.64	-202.89
0.5g/l	14.13	8.97	-202.44

In addition, the inhibition efficiency (IE) of the *piliostigma thonningii* leaves extract ranged from 97.84% to 88% (Table 1) inhibition efficiency (IE) increase gradually with the rise in concentration of the inhibitor but decreased with increase in temperature. Maximum inhibition efficiency of 97.84% was obtained at 0.5 g/l of leaves extract of *piliostigma thonningii* inhibitor in 0.5 M H_2SO_4 at temperature of 303K. Similar report has been reported in literature (Christov *et al.*, 2004).

h. Adsorption isotherm study

Adsorption is a surface process, which shows the linkage of a corrosion inhibitor between mild steel and *piliostigma thonningii* leaves extract in aqueous solution H_2SO_4 solution. The nature of the adsorption mainly depends on the inhibitor concentration and surface (ɵ) (El-nabil *et al.*, 2006). Adsorption isotherms were studied with the help of weight loss data for different concentrations of plant extract species at 303 K to 343 K. The study of adsorption process by applying different adsorptions models such as Langmuir, Temkin, Freundlich, and Flory- Huggins. All the plots exhibit straight lines and corresponding correlation coefficient (R^2) values are shown in table6. The best R^2 values (close to unity) observed in case of Langmuir adsorption model. Hence, Langmuir adsorption fits and significantly explains the adsorption process and results are shown in Table 6. According to Langmuir adsorption isotherm, ɵ is related to C_{inh} to the following equation:

Using the modified Langmuir expression shown below:

$$\frac{\theta}{1-\theta} = K_{ads}\, C_{inh} \qquad (7)$$

Where Θ is the surface coverage, K_{ads} is the adsorption- desorption equilibrium constant, C_{inh} is the concentration of inhibitor.

The rearranged Langmuir equation is: $\frac{C}{\theta} = \frac{1}{K} + C$ (8)

where Θ is the surface coverage, K is the adsorption- desorption equilibrium constant, C is the concentration of inhibitor (Huong *et al.*, 2019).

Langmuir plot of $\frac{C}{\theta}$ against C for various concentrations of *piliostigma thonningii* molecules by considering the Θ values from weight loss method. The obtained graph is shown in Figure 6. K_{ads} = Langmuir adsorption constant which describes the adsorption strength of an inhibitor on Mild steel surface.

The value of K_{ads} was obtained from the intercept of isotherm plot as shown in Table 6. It is well known fact that K_{ads} represents the strength between inhibitor molecules and mild steel. The higher the value of K_{ads} indicates the more efficient adsorption of the *piliostigma thonningii* on mild steel surface and hence better corrosion inhibition efficiency. The standard free energy of adsorption (ΔG°_{ads}) is calculated from slope of Langmuir adsorption isotherm using the fallowing equation:

$\Delta G^0_{ads} = -2.303RT \text{ Log } (55.5K_{ads})$ (9)

Where R is the universal gas constant (8.314J K^{-1} mol^{-1}), T is the absolute temperature (K) of the experiments and 55.5 is the molar concentration of water in the solution expressed in (mol L^{-1}). The interaction of *piliostigma thonningii* on the surface of mild steel can be classified into two types. If the ΔG°_{ads} = -20 kJ mol^{-1} or less that adsorption is physical adsorption or physisorption, while around -40 k J mol^{-1} or more that the chemical adsorption or chemisorption. In the present study, the ΔG°_{ads} values obtained are in order of -20 kJmol^{-1}. It indicates that *piliostigma thonningii* molecules and mild steel interaction is physisorption inevitably fallowed by chemisorption and the negative values $\Delta G_{ads}{}^0$ ensure the stability of the adsorbed layer and the spontaneity of the adsorption process (Gece *et al.*, 2008; Hmamou *et al.*, 2013; Chaouiki *et al.*, 2020).

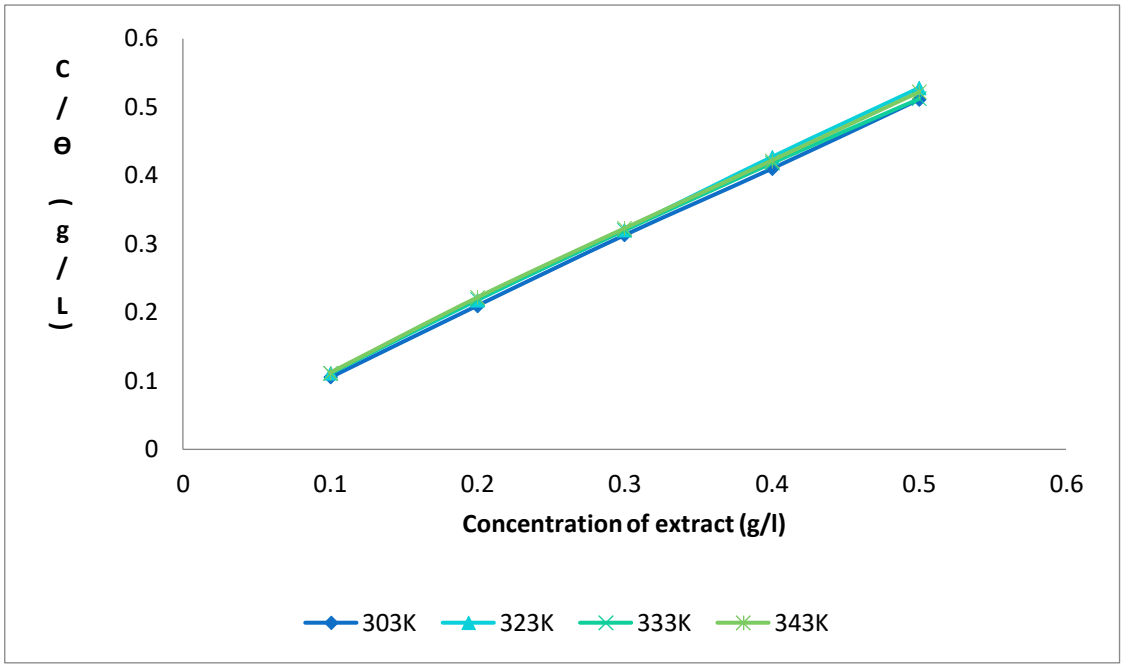


Figure 6: Langmuir plots for mild steel in H_2SO_4 solution inhibited with different concentrations of *piliostigma thonningii* leaves extract at various temperatures

Table 6. Langmuir Parameters for a Mild steel in 0.5 M H_2SO_4 Solution inhibited with different Concentrations of *Piliostigma thonningii* leaves extract at different temperatures

Tem (K)	Intercept	Slope	K_{ads} (10^4 M^{-1})	R^2	ΔG°_{ads} (Kj mol^{-1})
303	0.0062	1.012	161.3	0.999	-22.54
313	0.008	1.028	125	0.998	-23.02
323	0.0081	1.042	123.40	0.992	-23.71
333	0.0157	1.001	63.69	0.999	-22.62
343	0.0142	1.02	70.42	0.995	-23.59

Although determining Gibbs free energy is straightforward, it is subject to several limitations noted by various authors (Lrhoul *et al.*, 2023; Holla *et al.*, 2024; Bandeira *et al.*, 2025); the extract contains a

multitude of compounds at varying concentrations—rich in aromatics and heteroatoms that facilitate adsorption onto the metal surface—making the concept of an intermolecular synergistic effect essential.

i. Kinetic study

The corrosion reaction is a heterogeneous reaction, which is composed of anodic and cathodic reactions at the same or different rate. It is on this basis that kinetic analyses of a data are considered necessary. Corrosion of mild steel in the absence and presence of ethanolic extract with 0.3 g/L *piliostima thonningii* leaves extract, and uninhibited solution, was studied by fitting data into various kinetic model and it was found that a plot of In (W_1-W_2) versus time gave straight line graph with negative slopes indicating that the corrosion of mild steel is consistent with the following equation (Erdogan *et al.*, 2017).

For first order kinetics:

$$R = -d\frac{(WI - Wt)}{dt} \quad (10)$$

Integrated first order is given as:

$$\text{First order kinetics, } In\,(W_1 - W_t) = k_1\,t + In\,W1 \quad (11)$$

$$-\log(\text{weight loss}) = -k_1/2.303 \quad (12)$$

Where, W_1 is the initial weight of the mild steel, W_t is the weight after time t, K_1 is the first order rate constant, which has a unit of h^{-1}

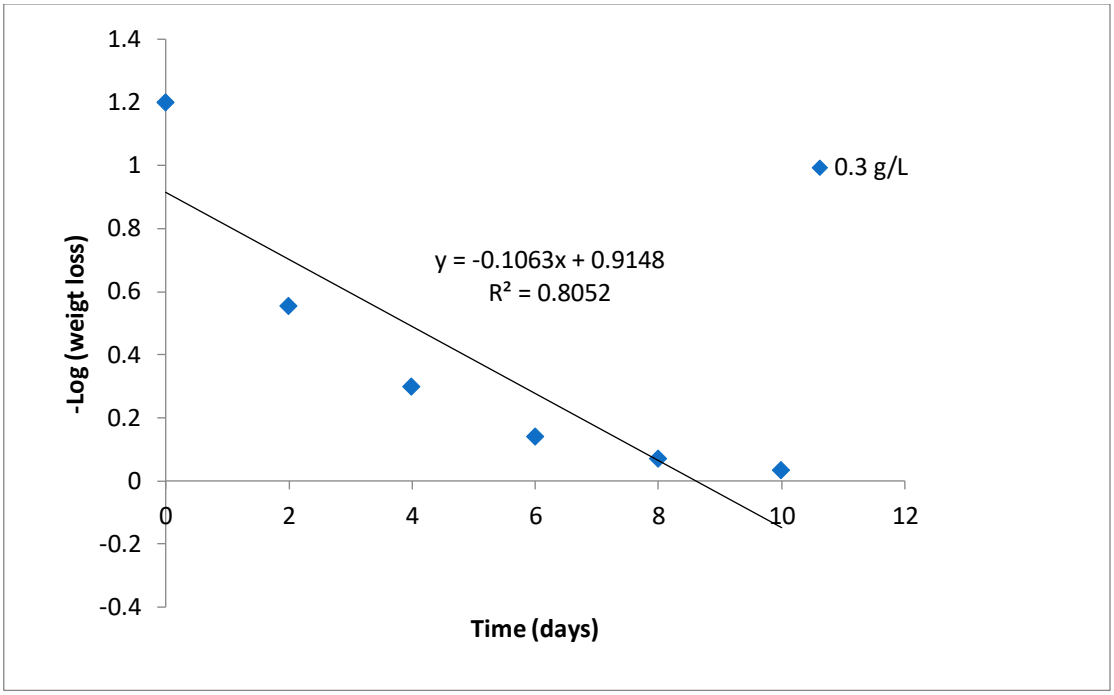


Figure 7. Variation of –log (weight loss) with time for the corrosion of mild steel in 0.5 M H_2SO_4 containing 0.3 g/L ethanol extract of *piliostigma thonningii*

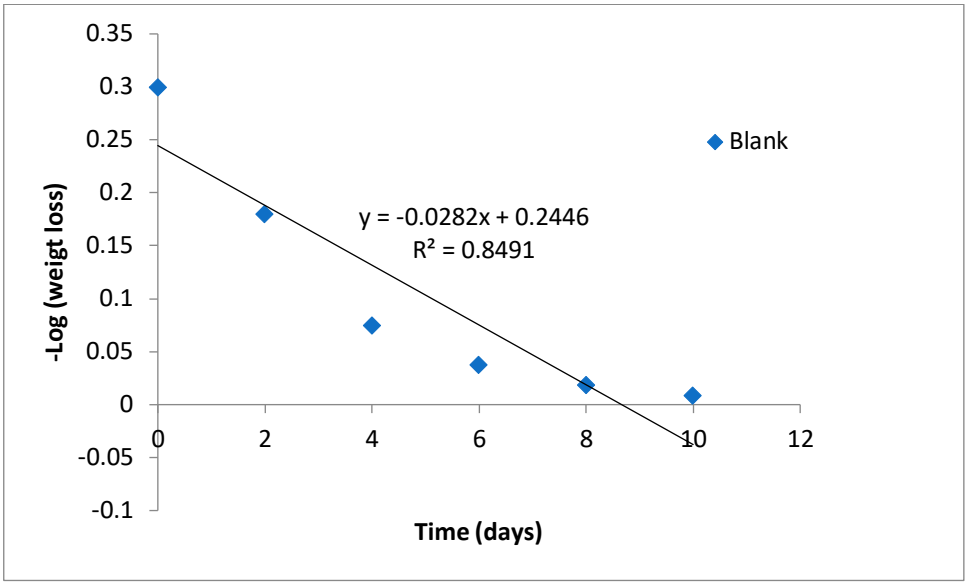


Figure 8. Variation of –log (weight loss) with time for the corrosion of mild steel in 0.5 M H_2SO_4 without inhibitor

Table 7. Kinetic Parameters for the Adsorption of Ethanol Extract of *Piliostigma thonningii* on Mild Steel Surface

Solution	Slope	k_1	R^2	$t_{1/2}$ (days)
Uninhibited	-0.1063	0.2448	0.8052	2.8
Inhibited	-0.0282	0.0649	0.8491	10.6

The value of rate constant (k_1) and correlation coefficient (R^2) deduced from the plots are presented in Table 8. The closeness of R^2 values to unity indicates that equation 7 is applicable for inhibition of mild steel in solutions of H_2SO_4 by *piliostigma thonningii*. Also, while the first order reaction, the half-life is related to the rate constant as follows

$$t_{1/2} = 0.693/k_1 \quad (13)$$

Results reported in Table 9 revealed that the half-life values for the blank were relatively lower than those for the inhibited medium which contained the plant extract with the immersed coupons of the mild steel (Fluentealla *et al.*, 2010).

Conclusion

Based on the above findings and discussion the fallowing conclusion are drawn:

- *piliostigma thonningii* leaves extracts exhibited good inhibiting characteristics against corrosion of mild steel in 0.5 M H_2SO_4 solution. This might be due to presence of adsorption of its phytochemical compounds in the leaves extracts that served as adsorption site onto the mild steel surface.

- Both gravimetric and electrochemical method showed inhibition efficiency of the leaves extract decreases with increase in the temperature and increased with increase in immersion period of mild steel in leaves extract.
- Langmuir adsorption isotherm best described the adsorption of leaves extract onto mild steel surface followed exothermic process and is spontaneous proposed from the obtained values of ΔG^0.
- SEM analysis reveals that the investigated inhibitor creates a smooth uniform surface on mild steel. In addition, the good inhibition tendency of inhibitor was further supported by the analysis of computational method.

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