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KINETIC AND THERMODYNAMIC ASSESSMENT OF THE POTENCY OF I*RVINGIA* GABONENSIS PLANT EXTRACT AS AN ECO-FRIENDLY INHIBITOR FOR MILD STEEL IN AN ACIDIC ENVIRONMENT

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Abstract

The kinetic and thermodynamic efficacy of Irvinga Gabonensis plant extract as an effective eco-friendly inhibitor for mild steel in acidic environment were studied using gravimetric measurement (GM) at varied temperature of 298,308, and 318 K, as well as scanning electron microscopy surface characterization, and were utilized. The findings indicate that Irvinga Gabonensis leaf extract inhibited acid-induced corrosion of MS effectively. The results of the kinetic analysis indicated that the inhibited species were more resilient. The extract's effectiveness as an inhibitor is determined by its concentration (C) and temperature (T). The active components of the extracts were found to adhere to the Langmuir adsorption isotherm, resulting in an adsorption-based inhibitory mechanism. It was also established from the study that the extract is a mixed-type inhibitor. SEM characterization further revealed that the surfaces were devoid of pits when the extract is present.

Keywords: *Thermodynamic; kinetic; mixed-type inhibitor; Irvingia Gabonensis; Phytochemical.*

Introduction

Engineers now have access to an extensive selection of structural materials owing to established and emerging technologies, allowing them to choose the ideal material for a specific use depending on the material's physical or mechanical qualities. Materials made of mild steel are essential to a nation's economic growth and long-term use in engineering industry. The interaction of this metal with its corrosive environment will always result in deterioration [1]. Due to the threats it poses to engineering structures and to industrial operations, awareness of corrosion effects [2,3] has increased. Prevention is the most effective method for combating corrosion [4, 5]. Corrosion is the degradation of metals in the presence of the environment. Therefore, additional research into corrosion protection methods for metals and alloys is necessary [6]. Corrosion of metals in aggressive solutions presents obstacles for acid pickling, industrial acid cleansing, acid descaling, and acidizing oil wells. In corrosive environments, corrosion inhibitors are frequently used to protect metals from further deterioration [7-13].

Inhibitors are applied to the surface of metal, where they form a thin coating and block corrosion. Most corrosion inhibitors on the market today are inorganic chemicals, some of which are rather dangerous due to the presence of nitrogen, sulphur, and oxygen. In recent years, there has been a shift towards producing natural corrosion inhibitor from plants and its derivatives,

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which is biodegradable and ecologically beneficial. The results of these studies [14-33] reveal that the use of these inhibitors has effectively halted corrosion. Nigeria is a tropical country; hence it has a rich variety of plant life. finding natural alternatives to the synthetic corrosion inhibitors now in use should be facile.

Irvingia Gabonensis leaves (IGL) plant is found within the Humid Forest zone in the northern parts of Angola, Congo, and Nigeria, and IGL plant is commonly used for medicinal purpose. This plant is found in the southern and eastern regions of Nigeria [34]. Analysing the kinetic and thermodynamic properties of *Irvingia Gabonensis* leaves (IGL) extract will allow the researchers to determine whether it is useful as a corrosion inhibitor for mild steel in an acidic environment. This will be done by evaluating the extract's effectiveness.

Experimental procedure

Materials

Mild steel (MS) with the constituents P (0.04%), Mn (0.8%), S (0.05%), C (0.16%), and Fe (98.95%) was subjected to corrosion testing. Before the corrosion process, the mild steel was mechanically cut into its desired shape. As described in [29], the coupon was polished with emery paper to enhance its lustre and degreased with acetone to remove any oil residue.

Preparation of extract

The *Irvingia Gabonensis* leaves (IGL) used was identified and purchased from Effurun market in Delta State, Nigeria. The fresh leaves were dried for five (5) days was then pulverized and kept for extraction. To create the extracts, 20 grammes of powdered desiccated leaves were refluxed for four hours in 1.0 M HCl and allowed to remain overnight. The products' filtrates were used as the stock solution. Using the filtrate, extract concentrations of 0.2, 0.4, and 0.6g/L were then obtained.

Gravimetric corrosion Analysis

The weight reduction procedure was performed at 298K, 308K, and 318K. As indicated previously [29,35], the difference between the initial and final weights of an unprotected and protected test solution was analysed. After the corrosion testing was finished, the coupons were removed and rinsed in acetone before being reweighed. The experimental data were recorded and analysed using equations (1)- (4) respectively as adopted from previous study [36].

$$\Delta W = w_i - w_a \quad (1)$$

$$\mathrm{CR} = \frac{W_{bl} - W_{inh}}{Area(m^2) \times Time(day)} \quad (2)$$

$$\mathrm{IE\%} = \frac{W_{bl} - W_{inh}}{W_{bl}} \times \frac{100}{1} \quad (3)$$

$$\theta = \frac{W_{bl} - W_{inh}}{W_{bl}} \quad (4)$$

where: W_i and W_a represent the coupon's initial and final weights, respectively. w_{bl} and w_{inh} represent, respectively, the weight loss values for the blank and inhibited conditions.

Phytochemical analysis

Irvingia Gabonensis leaves (IGL) phytochemical investigation was carried out to identify the reactive inhibitory metabolites in the extract, including alkaloids, saponins, tannins, and flavonoids etc.

Surface Morphology

A Jeol JSM-7600F UHR Analytical FEG SEM machine was used to examine the surface morphology of both blank and inhibited mild steel.

Results and Discussion

Weight loss (WL) measurements

The weight loss (WL) of Mild steel (MS) in 1.0 M HCl using 0.2, 0.4, and 0.6 g/L of IGL extract and varying immersion durations (8-24h) and temperatures (298, 308, and 318K). WL, CR, and IE were derived using Equations 1, 2, and 3 from the obtained values. Figures 1, 2, and 3 depict the WL, CR, and IE plots, respectively.

Fig. 1 illustrates the results of using Equation 2 to calculate the weight loss of mild steel at various inhibitor concentrations. According to the study's findings, the inhibitor substantially slowed the mass loss of metal coupons compared to the blank condition. In addition, it was demonstrated that an increase in inhibitor concentration decreased coupon weight loss. At higher inhibitor concentrations, a greater number of inhibitor molecules are deposited on the surface of mild steel metal, resulting in greater coverage of the metal's surface by the inhibitor, thereby making it exceedingly difficult for corrosion to continue. When the IGL extract inhibitor was absent, mild steel lost significantly more mass than when it was present.

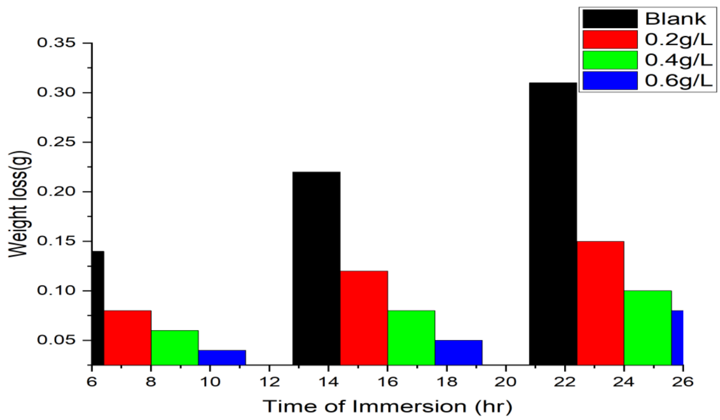


Fig. 1. Weight loss against time of immersion

Fig. 2 depicts the correlation between corrosion rate and immersion duration in HCl solution (without and with inhibitor).When the *Irvingia* Gabonensis leaves (IGL) extract inhibitor was present, the corrosion rate of mild steel decreased, according to the results. As inhibitor concentration increased, the rate of corrosion decreased.

In-depth analysis of Fig. 3 revealed that the concentration of *Irvingia* Gabonensis leaves (IGL) extract influenced directly the degree of inhibition generated by the spontaneous attachment of active IGL molecules, which acts as a barrier to mass transfer processes and halts further dissolution[31].At a concentration of 0.6 g/L, the greatest inhibition (92,3 %) was observed. Since the presence of a dense metal-inhibitor interaction between the adsorbate (IGL) and the steel surface prevents chloride ions (Cl) from adsorbing on the steel surface, the adsorption mechanism between the adsorbate and the steel surface is well established. The results indicate that due to the presence of active metabolites, IE increased as the concentration of the IGL extract increased.

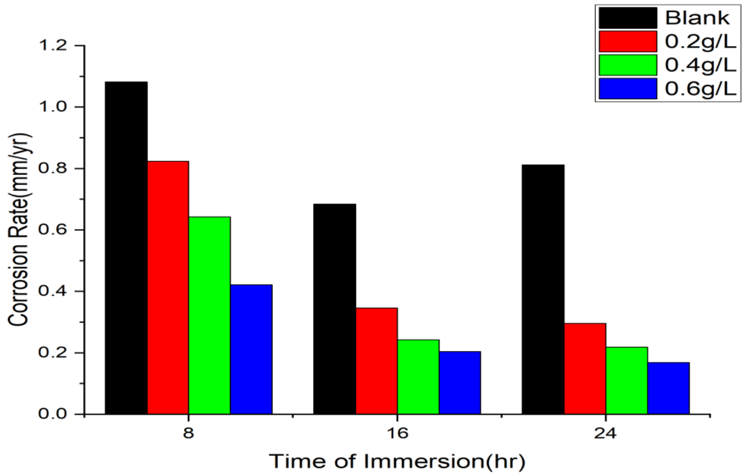


Fig. 2 Corrosion rate against time of immersion

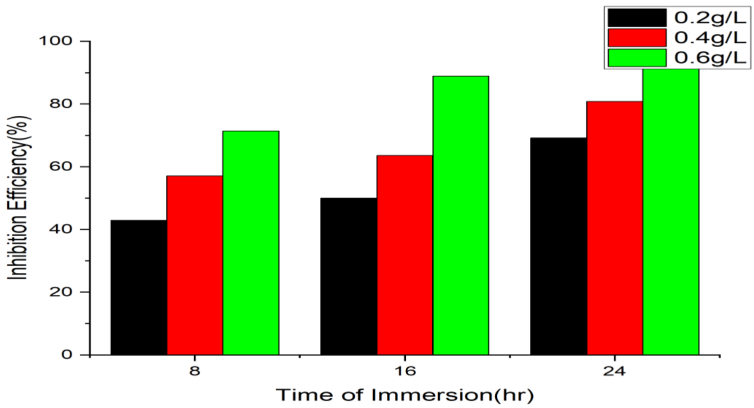


Fig. 3. Inhibition Efficiency against immersion time

The efficacy of *Irvingia Gabonensis* leaves (IGL) extract to prevent corrosion of mild steel in a 1.0M HCl solution was investigated over the course of 24 hours at concentrations of 0.2g/l, 0.4g/l, and 0.6g/l inhibitor at temperatures ranging from 25 °C to 45 °C. Fig. 4 depicts the effect of temperature on corrosion rate in the absence and presence of inhibitors. Corrosion occurs more rapidly in the absence of an inhibitor than in the presence of one. At elevated temperatures, the extract's inhibitor molecules lose their ability to adsorb onto the ductile steel, which explains why corrosion accelerates under such conditions [46].

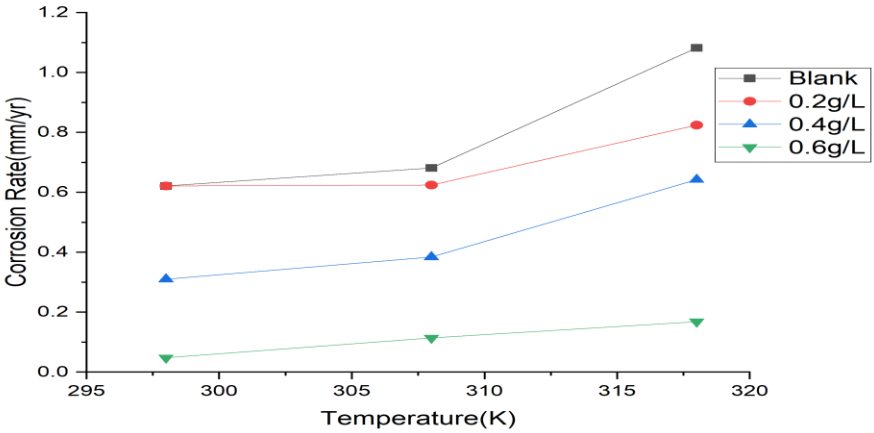


Fig. 4. Effect of Temperature on rate of corrosion of mild steel

Adsorption studies

The adsorption at the metal/solution interface is related to the effectiveness of an extract as a corrosion inhibitor in highly acidic environments. According to [37], for the extract to be effectively adsorbed onto the metal surface, the synergistic force between the metal and the water molecule must be less than the reciprocal force between the metal and the extract. Consequently, the adsorption isotherm can be used to describe the corrosion-prevention processes. The Langmuir Isotherm was used to analyse the corrosion adsorption processes of the *Irvingia gabonensis* leaves(IGL) extract on the mild steel surface in a 1.0M HCl solution. The plot of $\frac{C}{\theta}$ against concentration (C) for the Langmuir isotherm using equation 5 was used to obtain the values of K_{ads} at different temperatures.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{5}$$

where: C is the inhibitor concentration in grams per liter, K_{ads} is the adsorption-desorption equilibrium constant in g/L, and is the surface coverage.

Table 2 displays the calculated K_{ads}, slope, and intercept of the straight lines depicted in Fig. 5 at respective temperatures of 298 K, 308 K, and 318 K. The Langmuir adsorption isotherm [30] relies on the following assumptions, for coverage to have no effect on the typical adsorption-free energy, the metal surface must be uniform, the adsorbate must occupy a single surface site, and the adsorbed compounds must not diffuse across the metal's surface. For temperatures of 308 K and 318 K, the Langmuir isotherm equation produces straight lines with gradients that are not exactly equal to unity, with R^2 = 0.9934, 0.9932, and 0.9996, respectively. Even though the R^2 values are consistent with the Langmuir adsorption isotherm, the gradients contradict the notion that inhibitor molecules are adsorbed in a monolayer on the surface of the adsorbent.

Inhibitor adsorption in monolayers, for instance, is independent of temperature and requires homogenous metal surfaces with no dispersion of the adsorbed molecules [38-40]. This may be why data from typical metal inhibition processes do not align the Langmuir adsorption isotherm. Even for a prototypical acid inhibition system like the one under consideration, the presence of foreign ions and their interactions in the same medium renders these assumptions unlikely. Depending on the potential, some adsorption processes may be selective with regard to the categories of charges present on the metal surface.

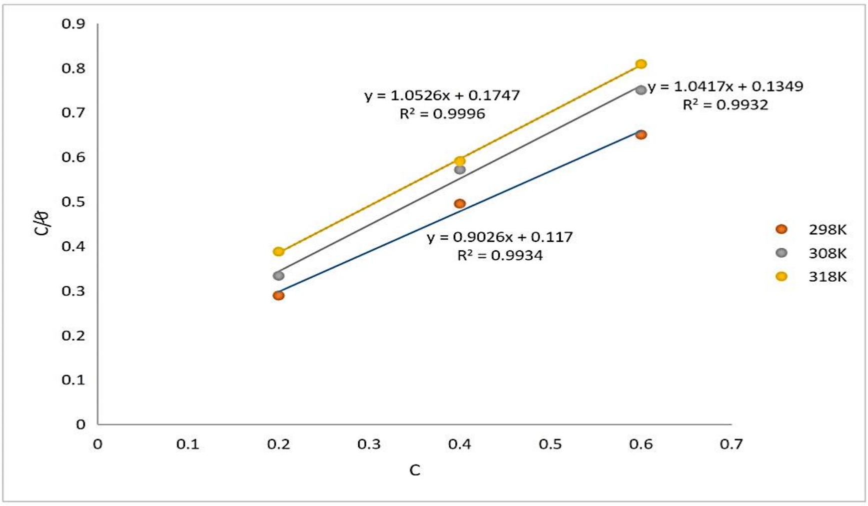


Fig. 5. Langmuir adsorption plot of $\frac{C}{\theta}$ and extract concentration (C) for mild steel at 0.2–0.6 g/L of IGL extract

Table 2. Langmuir adsorption parameters for the adsorption of leaves extract of IGL on the surface of the mild steel.

Temperature(K)	Slope	Intercept(g/L)	K_{ads} (L/g)	R^2	ΔG^0(kJ/mol)
298	0.9026	0.117	8.55	0.9934	-22.43
308	1.0417	0.1349	7.41	0.9932	-22.82
318	1.0526	0.1747	5.72	0.9996	-22.87

According to [38-40], these deviations from the standard adsorption isotherm have implications for the adsorption process and must be explained by considering another physical characteristic of the isotherm. This dimensionless separation constant (K_L) may be incorporated into the Langmuir adsorption isotherm as shown by Equation (6).

According to [38-40], another physical characteristic of the adsorption isotherm must be considered in order to comprehend these phenomena and how they influence the adsorption process. To incorporate the K_L into the Langmuir adsorption isotherm, it is generated mathematically as shown in Equation (6).

$$K_L = \frac{1}{1+K_{ads\,C}} \tag{6}$$

where: K_{ads} denote the adsorption equilibrium constant, K_L is the dimensionless separation factor of the extract, and C is the concentration of the extract.

Table 3 displays the predicted K_L values for mild steel in 1 M HCl at 308 and 318 K for different concentration of *Irvingia* Gabonensis leaves (IGL) extract. For K_L values > 1, adsorption is unfavourable and contradicts the Langmuir adsorption isotherm. While $K_L = 1$ and $K_L = 0$ indicate linear and irreversible adsorption, respectively, for $K_L < 1$, adsorption is favourable and experimental data are in accordance with the Langmuir adsorption isotherm [40]. Table 3 shows that the adsorption process is characterized by a Langmuir isotherm, with all K_L values for inhibitor concentrations being less than unity.

Table 3. K_L values for corrosion of mild steel in 1 M HCl as a function of IGL extract concentration at temperatures of 308K and 308K.

	K_L	
Conc (gL^{-1})	**308K**	**318K**
0.2	0.403	0.47
0.4	0.25	0.30
0.6	0.18	0.23
Mean	0.23	0.33

$$K_{ads} = \left(\frac{1}{C_{solvent}}\right)\exp\left(\frac{-\Delta G^0}{RT}\right) \tag{7}$$

where: R is the molar gas constant in J/mol, T is the absolute temperature in K, $C_{solvent}$ is the concentration of water in solution in g/l, and K_{ads} is the adsorptive/desorptive equilibrium constant in L/g, all determined from the intercept of Fig. 1. ΔG^0 is the adsorption free energy in KJ/mol. It is quite clear that the function of K_{ads} correspond to the unit of $C_{solvent}$. As shown in Table 1, Table 1 reveals that K_{ads} is expressed in L/g, so $C_{solvent}$ has a value of approximately 1.0×10^3 [41, 42].

The values for ΔG^0 are all negative, indicating that the molecules of the extract have autonomously adsorbed, as shown in Table 2. The ΔG^0 values imply a distribution of heterogeneous absorption. The calculated ΔG^0 values of -22.43, -22.82, and -22.87 kJ mol shown in Table 2 for temperatures of 298, 303, and 333K, respectively, ΔG^0 values below 20 kJ mol are consistent with electrostatic interaction between the organic molecules and the metal surface (physisorption); ΔG^0 values above 40 kJ mol require charge sharing or transfer from the organic molecules to the metal surface (chemisorption) [43, 44]. IGL extract contains a variety of chemical components [34], some of which may adsorb chemically and others physically; these components vary with temperature [45]. It is therefore possible that this is the physiochemical mechanism underlying the dual mode of adsorption.

Kinetic and Thermodynamic Studies

The kinetics study of corrosion of MS in 1.0 M HCl solutions involves inputting values derived from the computation of weight loss into multiple kinetic models. The assessment reveal corrosion of MS in HCl solution aligns with the first order kinetic model.

According to [46], the kinetic equation of the reaction can be represented by Eq. 8 if the initial concentration of Fe in the mild steel is a_0 and x moles of the corrosion product are produced after t time.

$$\frac{dx}{dt} = \mathrm{k1}(a_o - x) \tag{8}$$

where: k1=first order reaction rate constant. Rearrangement of Eq. 8 gives Eq. 9 which upon integration, lead to Eqs. 10 and 11 respectively.

$$\frac{dx}{(a0 - x)} = K_1 \mathrm{dt} \tag{9}$$

$$-\mathrm{In}(a_0 - x) = K_1 t \tag{10}$$

$$-\log(\text{weight loss}) = \frac{K_1 t}{2.303} \tag{11}$$

$$t_{1/2} = \frac{0.693}{k_1} \tag{12}$$

Table 4 and Fig. 6 show that the half-life of mild steel in 1 M HCl with *Irvingia* Gabonensis leaves (IGL) extract is greater than in the blank solution. Until the optimal concentration of the extract was attained, the half-life was observed to increase with its concentration. Table 4 demonstrates that as concentration increases, the first order rate constant decreases. Thus, the half-life and the rate constant of the first order are discovered to be inversely proportional. Therefore, it has been demonstrated that the presence of IGL extract in the aggressive solution increased the service life of mild steel [33-36].

Table 4. Kinetic parameters obtained varying concentration of the various concentration of IGL extract

Inhibitor Concentration(g/L)	Corrosion Rate(mm/y)	Efficiency (%)	Surface Coverage (Θ)	First Order Rate Constant	Half life	R^2 value
Blank	1.082	0	0	0.0216	32.08	0.9938
0.2	0.824	42.7	0.429	0.0171	40.53	0.9973
0.4	0.168	72.4	0.724	0.0139	49.86	0.9947
0.6	0.048	92.3	0.923	0.0112	55.89	0.9964

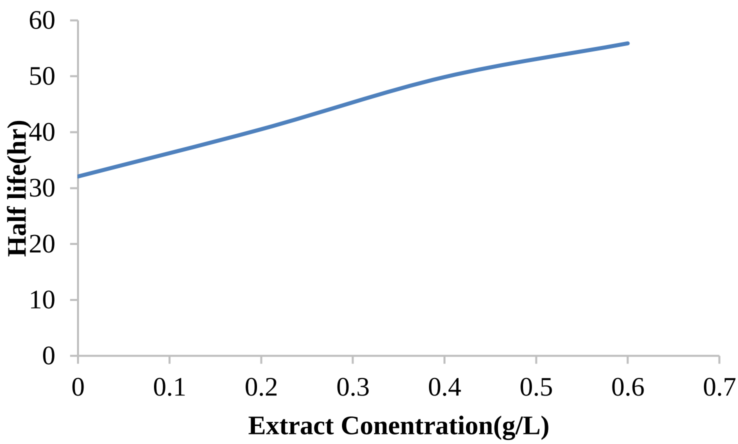


Fig. 6. Relationship between half life and extract concentration for mild steel at varying concentration of the various concentration of IGL extract.

Using the logarithmic form of the Arrhenius equation [47,51], as shown below, we analysed the effect of temperature on MS corrosion in a 1.0M HCl blank acid solution with variable concentrations of the extract.

$$\text{In}\left(\frac{C_{R2}}{C_{R1}}\right) = \left(\frac{E_a}{2.303R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (13)$$

where: CR_1 and CR_2 represent corrosion current densities in millimetres per year, T_1 and T_2 represent temperatures in Kelvin, Ea represents the apparent activation energy for the reaction in kilojoules per mole, and R represents the molar gas constant in joules per mole.

The E_a for mild steel protection using *Irvingia gabonensis* leaves (IGL) extract in HCl solution is shown in Table 5. The table below demonstrates that the computed Ea values for the inhibited solution containing IGL extract range from 22.02 to 39.54KJmol^{-1} for an inhibition concentration between 0.2 and 0.6g/L. This study demonstrated that a film layer adsorbing onto the metal surface delayed MS partial reactions in the inhibitor solution by a significant amount.

The heterocyclic compounds in the IGL extract inhibit further metal dissolution, making the film layer more resilient than the surface deterioration of the metal [52].

Using the transition state equation, various thermodynamic parameters (ΔH_{ads} and ΔS_{ads}) were calculated for the adsorption of IGL extract on the surface of mild steel.

$$\mathrm{CR} = \frac{\mathrm{RT}}{\mathrm{Nh}}\exp\left(\frac{\Delta S_{ads}}{R}\right)\exp\left(-\frac{\Delta H_{ads}}{RT}\right) \tag{14}$$

Using the equation: CR = corrosion rate, R = gas constant, T = temperature, N = Avogadro's number, h = Planck constant for mild steel dissolved in 1M HCl ,ΔHads represents the enthalpy of adsorption of the inhibitor onto the surface of mild steel, while ΔSads represents the entropy of adsorption. Equation 15 was derived by taking the logarithm of both sides of Equation 14.

$$\mathrm{Log}\frac{\mathrm{CR}}{\mathrm{T}} = \mathrm{Log}\frac{\mathrm{R}}{\mathrm{Nh}} + \frac{\Delta S_{ads}}{2.303R} - \frac{\Delta H_{ads}}{2.303RT} \tag{15}$$

Table 5 provides a summary of the ΔH_{ads} and ΔS_{ads} values computed. This result strongly suggests that the extract slowed the energy barrier of the corrosion reaction without altering the depletion process of the metal [43]. Table 5 reveals that the enthalpy of adsorption, H_{ads} , is positive, indicating that the dissolving mechanism of MS is endothermic and consequently slow [41,42]. Furthermore, both in the absence and presence of *Irvingia* Gabonensis leaves (IGL) extract, the entropy of adsorption, ΔS_{ads} is negative, indicating that the association phase, not the dissociation phase, is the phase that determines rate for the activated complex. Adsorption of the extract onto the surface of the adsorbent was accompanied by a decrease in entropy, which is the propelling force for the adsorption of the leaves extract onto the MS surface [53]. This is demonstrated by the increasing negative value of the entropy of adsorption, ΔS_{ads} , as the extract was added (Table 5).

Table 5. Thermodynamic parameter obtained varying concentration of the various concentration of IGL extract

Inhibitor concentration	Activation Energy (*Ea*)	Enthalpy of adsorption (ΔH_{ads})	Entropy of adsorption (ΔS_{ads})
Blank	19.71	19.17	-105.12
0.2	22.02	28.47	-142.9
0.4	28.54	27.01	-165.37
0.6	39.54	46.99	-181.92

Phytochemical Analysis

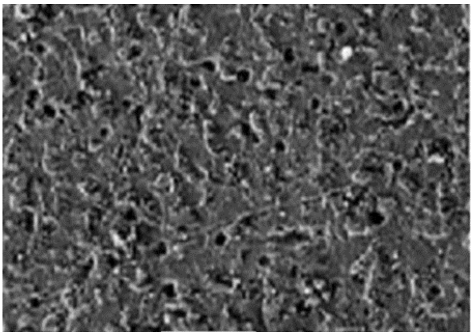
Table 6 below highlights the bioactive compounds present in the IGL extract. These include tannin, flavonoids, saponin, alkaloids, and resins. Tannins have been demonstrated to be the most potent biochemical inhibitors present. These phytochemicals have shown to enhance the corrosion resistance of mild steel in an acidic environment [34]. It has been discovered that the presence of these compounds in the IGL extract enhances the corrosion inhibition of mild steel in HCl solution.

Table 6. IGL phytochemical constituents (+++ = highly present; ++ = moderately present; + = present).

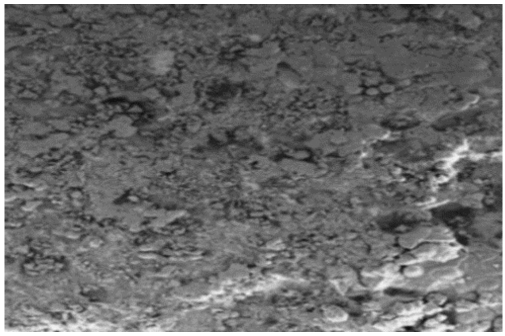
Biospecies	Confirmation
Alkaloids	+
Tannins	+++
Flavonoid	++
Saponins	++
Resins	++

SEM Study

The MS surface was severely corroded in the 1.0 M HCl solution without IGL extract (Fig. 7(a)), but *Irvingia gabonensis* leaves (IGL) extract mitigated the corrosion (Figures 7(b) and 7(c)). This indicates that a layer of protection was formed on the mild steel surface because of the adsorption of inhibitor molecules. This result is consistent with those found in the literature [54–56].



a)



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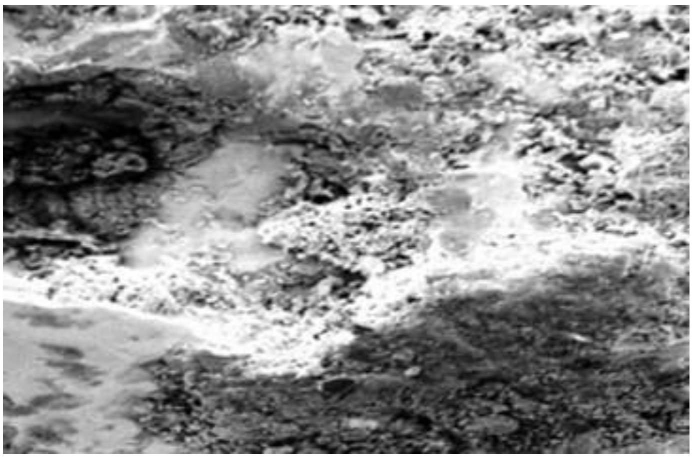

c)

Fig. 7. SEM micrographs of mild steels after corrosion in 1 M HCl containing IGL extract at 45 ºC: a) without inhibitor; b) 0.2g/L Conc. of IGL inhibitor; c) 0.6g/L Conc. of IGL inhibitor.

Conclusion

The inhibition of mild steel corrosion in a 1.0M HCl solution by IGL extract was investigated. When the extract was added to the acidic solution, the corrosion rate was reduced, surface coverage was increased, and the half-life of the inhibited samples was significantly increased. The extract acted as a hybrid inhibitor, as determined by the adsorption test results. Both extract concentration and temperature were found to enhance the inhibitory efficacy of the extract. The evaluated activation and thermodynamic parameters demonstrate that the adsorption of IGL extract on MS is endothermic and occurs via chemisorption at elevated temperatures and physisorption at lower temperatures. In addition, the negative entropy value indicates that the reaction occurred spontaneously. The adsorption mechanism is consistent with Langmuir adsorption isotherms. The surface morphology of inhibited specimen reveal is more smoother surface devoid of pits compared to the blank specimen.

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