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Cathodic corrosion inhibition of Steel by Musa paradisiaca leave extract

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Abstract

It is reported here that the phytochemicals present on the surface of the *Musa paradisiaca* (MPL) prevent water and other corroding agents from having direct access to the surface of mild steel. These phytochemicals were extracted from the MPL using 70% Ethanol solution and Weight Loss experiment was carried out with variation of temperature, time and concentration *HCl* and that of the MPL extract in % *v/v*. The inhibitive effect of *M. paradisiaca* leaves of mild steel in aqueous solutions of Hydrochloric acid were investigated at 25, 35, 45 and 60 °C being immersed simultaneously and independently in the acid medium over a period of 12, 24, 48, and 72 hours. A protecting film appeared on the metal surface by the MPL extract via electron donation, hence, acting as the cathode. The temperature and immersion time were inversely proportional to inhibition efficiency while concentration of MPL is directly proportional. FT-IR of the extract showed oxygen and nitrogen containing functional groups which are the general characteristics of a typical corrosion inhibitor, while the Gas Chromatography–Mass Spectrometry (GC–MS) investigation revealed different biomolecules thus suggesting that the plant extract consists of different molecules.

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Keywords: Corrosion, corrosion inhibitor, desorption, green chemistry, M. paradisiaca, mild steel

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1. Introduction

Corrosion of metals has been around us even before industries came to existence and the need for the prevention or cure has been a major problem. Aggressive acids such as HCl are frequently utilized to eliminate mild scale and rust found in iron and steel in chemical industries [1]. These inhibitors were utilized by the industries for their anti-corrosive properties but

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they cause some adverse effects on the environment. This has resulted in the synthesis of corrosion inhibitors that are environmentally affable and are called Organic Corrosion Inhibitors (OCI) [2]. Corrosion Inhibition can be carried out by the use of organic or inorganic approach. The organic approach is also known as Green Corrosion Inhibition which is one of the bestknown corrosion safety techniques [3-5]. The use of extract of natural product as inhibitor of corrosion was first evidence in 1930 whilst extracts from *Chelidonium majus* and some other plants were utilized in Sulfuric acid, H₂SO₄ medium for the first time [6-7]. With this, there is no or minimal amount of

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pollution caused and it is cost efficient since these are extracts from plants that can be easily isolated.

Organic compounds with effective corrosion inhibitors often contain conjugated systems, and conjugated aliphatic bonds due to the presence of lone pairs of electrons (N, O, S and P), in aromatic rings, and pi-electrons, often have ionizable parts which are either hydrophilic or hydrophobic in nature [6, 8-10]. More research and developments are emerging in the study of natural corrosion inhibitors as need for environmentally friendly inhibitors are gaining ground. For example, Cr₂O₃ which is insoluble in aqueous media that span across acidic and basic pH range and its susceptible to the underlying metal, it may serve as a barrier to corrosion [11]. Hexavalent chromium has shown to persuade irrevocable health challenges through skin irritation, nose, throat and eye and most importantly raises the alarm of lung cancer [12]. For application in coatings and primers, a comparable universal anti-corrosion compound has yet to be found, so that the need for chromate substitutes and ways of deployment of corrosion protection spans many industries. Drugs had been studied as corrosion inhibitor at some time [13]. Over the decades, green chemistry has shown how basic scientific approaches can benefit from the conservation of the human health and that of the environment by combining areas such as polymers [14-15]. Awareness to corrosion and the adaptation of fast, appropriate and accurate control measures holds the key in the eradication of corrosion failures. Heterocyclic molecules show essential behaviour as anti-corrosion owning to the available of sulfur, oxygen, and nitrogen atoms in either open or in their ring structure. However, no much works had provided detailed study on the mechanism of corrosion inhibition by these heteroatoms or heterocyclic molecules. In this work, extracted phytochemicals from MPL were used as green corrosion inhibition to decrease the rate of corrosion of steel in acidic medium. GC-MS and FT-IR investigations were carried out to examine the composition of the corrodent. The concept of Crystal Field splitting was deployed to provide lucid interpretation of the corrosion mechanism. Isotherms and thermodynamics were deployed to investigate corrodent sorption onto the steel surface.

2. Materials and Methods

2.1. Preparation of Metal Coupons

The specimen of mild steel was sliced into rectangular coupons by lathe machine into dimension of 20.21 *mm* by 14.63 *mm*. The coupons with its edge were polished with emery paper of 600 *grades*. The thickness was examined with Mitutoyo brand of analog micrometer screw gauge and the dimension by Mitutoyo digital venier gauge. The surface of the coupons was degrease through immersion in absolute ethanol and then removed for rinse with double distilled water and acetone and thereafter stored in moisture free desiccators before use [16].

2.2. Preparation of Plant Extract and Cold Extraction Process

Fresh *Musa Paradisiaca* leaves (MPL) were gathered in large quantities, selected from around same source, to ensure no con-

taminated leaves of different plant or specie. The impurities associated with the leaves were removed through tap water washing and thereafter air-dried to constant weight. It was shredded into smaller pieces to increase drying rate and thereafter dried for 3 weeks. Using 70% ethanol for solvent extraction at room temperature, the pulverized sample of MPL was soaked for 48 hours until a dark-green color was observed indicating that extraction has taken place. The darkish-green solution was filtered out which contains the plant extract while the residue is the chaff from pulverized leaves. The procedure was repeated on the chaff to ensure maximum extraction. The filtrate was refluxed to ensure homogeneity of the sample. The concentration of the extract of plants was carried out using a Rotary Evaporator which removes solvents from the extract thereby making it slurry. The concentrated and purified extract was then stored in desiccator.

2.3. Plant Extract Structural Elucidation

2.3.1. Gas Chromatography Mass - Spectroscopy (GC-MS) Investigation

A 7820A gas chromatograph coupled to 5975C inert mass spectrometer was used for this analysis. Scanning of potential compounds was at 2.62 *s/scan* rate and was recognized by comparing detected spectral data with NIST 14 Mass Spectral Library standard [17].

2.3.2. FT-IR Analysis

The functional group evaluation was done using Fourier transform infrared spectroscopy (FT-IR) model 8400S (Shimadzu, Japan). A mortar and pestle were used to mixed the MLP and KBr in the ratio of 1:99% and pestle and compressed into pellets. The FT-IR spectrums were determined from 400 cm⁻¹ to 4000 cm⁻¹ at a resolution and times scanning of 4 and 64 respectively.

2.3.3. Weight Loss Experiments

Mild steel of 20.21 mm by 14.63 mm were used for weight loss measurement. The total geometric of the coupon's surface area available to the corroding agent was about 295.67 mm² and average weight of coupons was 13.18 to 15.61 grams. The weighed coupons were immersed in 20 mL sample bottles containing concentration of corroding agent, HCl to that of the extract (*Musa paradisiaca*) as: 20:0 ν/ν , 15:5 v/v, 10:10 v/v, 5:15 v/v at 25 ± 2 °C and 60 °C consecutively for 72 hrs. This procedure is repeated further for 1.0 M and 2.0 M of HCl at 60 °C. Experiment on weight loss was used to estimate the inhibition efficiency, rate of corrosion and also the half-life of the metal coupon.

3. Results and Discussion

3.1. Fourier Transform Infrared (FT-IR) Analysis

Investigation on the various functional groups in the plant extract was determined using FT-IR. In the FT-IR spectra shown in Figure1 below, it revealed absorption bands belonging to the N-H and O-H bands which occured between 3325 - 3567



Figure 1. Musa Paradisiacal Leaves FT-IR spectrum

cm⁻¹, while the C-H stretching vibrations was noted between 2378 - 2987 cm⁻¹. The vibration of C=C stretching occured at around 1645 cm⁻¹, while that corresponding to C-N vibration stretching was observed at 1248 cm⁻¹. The absorption vibrations which occurred between 1098 and 1102 cm⁻¹ are due to C-O functional group. FT-IR of the extract showed that oxygen and nitrogen atoms were present in the plant extracts which is the general characteristics of a typical corrosion inhibitor. Table 1 shows the different functional groups present on the plant extract.

Table 1. Musa Paradisiacal Leaves Extract FT-IR Analysis				
Vibration mode				
O-H and N-H				
C-H				
C-H				
C=C				
Methyl C-H				
C-N				
C-O				

GC-MS examination of the corrosion inhibitor revealed different biomolecules thus suggesting that the plant extract consists of different molecules as listed in Table 2 with the microgram shown in Figure 2. As identified from the GC-MS analysis, the compounds which could be responsible for the weight loss are 6-Amino-1,3,5-triazine-2,4(1H,3H)- dione, 9-Octadecenamide, (Z)- Ole amide, Polygalitol, Cyclotetrasiloxane, octamethyl-, Thiophene, 2,3-dihydro- and Ginsenol repectively. It should be noted that O, N or S and/or p-electrons are present in most of the biomolecules identified from the extracts of the plant. From the GC-MS investigation, the compound which mostly has more inhibition is Ginsenol with time retention of 24.063. The inhibition of the rate of corrosion by MPL extract could be assigned to the presence of these phytochemicals which are made up of S, N, O, and other heteroatoms in their structures which are responsible for donating electrons to inhibit the corrosion process and thus serving as adsorption points on the surface of the metal.

3.2. Weight Loss Determination of Extract Inhibition

The metal weight loss during the experiment can be calculated as shown in equation 1 [18]:

$$\Delta W = (W_i - W_i)g \tag{1}$$

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Given that ΔW is the coupon weight loss, the initial coupon weight is denoted as W_i , the final coupon weight is given as W_f . The corrosion rate is estimated as:

$$CR, \rho = \frac{Weight_Loss}{(Surface_Area)} \times Time$$

$$= \frac{\Delta W_t}{S}$$
(2)

where CR= ρ and is corrosion rate $gcm^{-2} min^{-1}$ or $gcm^{-2} hr^{-1}$, ΔW is weight loss, S is Surface area, and t is immersion period.

The inhibition efficiency can be obtained by using equation 3a or 3b

$$I.E.\% = \left[\frac{W_u - W_i}{W_u}\right] \times 100 \tag{3a}$$

$$I.E.\% = \left[\frac{\rho_1 - \rho_2}{\rho_1}\right] \times 100 \tag{3b}$$

such that *I.E.* is Inhibition Efficiency, W_u is Weight of uninhibited mild steel surface, W_i = Weight of inhibited mild steel surface, ρ_1 is rate of rate of uninhibited corrosion, and ρ_2 is the rate of inhibited corrosion.

For calculating Percentage extract yield,

$$\%Extraction Yield = \frac{W_1 - W_2}{W_1} \times 100$$
(4)

where W_1 is weight of extract before extraction and W_2 is weight of extract after extraction. Surface coverage determination for Isotherm calculations is given as:

$$\theta = \frac{I.E}{100} \tag{5}$$

given θ is the surface coverage and *I.E.* is Inhibition Efficiency.

3.3. Effect of MPL extract Concentration

The MPL extract concentration is the variation in volume of the corrodent to the acid used, HCl, to make a volume of 20 mL. The experiment indicates a reduction in rate at which corrosion occur, thereby increasing inhibition efficiency (Figure 3). This also was calculated by comparing a medium with only the acidic medium and another containing the MPL extract, even with temperature variation, the result was still relative. It was established that the best inhibition efficiency was gotten from 5-15% v/v which is 5 mL of the acid and 15 mL of the plant extract. And the highest corrosion rate was seen on 20-0% v/v. As shown in Figure 3 below, the corrosion rate is inversely proportional to the concentration of the MPL extraction. Moreover, corrosion rate is the inverse of inhibition efficiency.



Figure 2. GC-MS Chromatogram of MPL extract

Retention	Name	Formula	Molecular	Estimated
time				Conc.
			$(g.mol^{-1})$	
6.841	6-Amino-1,3,5-triazine-	$C_3H_4N_4O_2$	127.29	27
	2,4(1H,3H)-dione			
6.841	9-Octadecenamide, (Z)-	C ₁₈ H ₃₅ NO	281.477	98
	Ole amide			
12.726	Polygalitol	$C_{6}H_{12}O_{5}$	164.16	49
9.324	Cyclotetrasiloxane,	$C_8H_{24}O_4Si_4$	296.6152	87
	octamethyl-			
8.475	Thiophene, 2,3-dihydro-	C_4H_6S	86.16	50
24.063	Ginsenol	$C_{15}H_{26}O$	222.3663	38

Table 2 Molecules extracted from the GC-MS Chromatogram of MPI

3.4. Effect of Immersion Time

The variation of inhibition performance of *Musa paradisiacal* leave extract as well as the corrosion rate with immersion time at concentration of 5-15% v/v is shown Figure 4. It was observed that the corrosion rate increases with the immersion time until 72 *hour*. A best immersion time of 12 hours was perceived for the whole concentration gradient of the inhibitor. Marginal inhibition sets in after the 48 hours due to desorption which occurs with prolonged exposure of the inhibitor to the acid medium, the corrosion rate tend to decline more rapidly than normal. And I.E. was noticed to have decreased with increased immersion time, this phenomenon could be blamed on desorption of the plant extract which initially prevent corrosion from taking place and also, at initial stage of the immersion, the inhibitory efficiency of the active components of the plant is high but as the reaction proceed, these active components are used up or destroyed; thus giving rise to increase in corrosion rate. More also, the presence of the corroding agent over long time made the corrosion abundant. Not forgetting that adsorption is by Van der Waal forces of attraction, and they are easily reversible [19], by stress. This stress may include pressure, temperature, current, etc. but on this case, it is caused by temperature and long exposure to the corroding agent. According to Ascencio *et al.* [20], he reported the influence of immersion time on corrosion mechanism and there is an inclination from this study.

Δ



Figure 3. Effect of *Musa paradisiaca* concentration on the inhibition efficiency and corrosion rate



Figure 4. Effect of time of immersion

3.5. Effect of Temperature

Inhibitors desorption or decomposition of the inhibitor with increase in temperature are some of the changes that occur on the metal surface [21-23]. Variation in CR at different concentration of MPL extract was examined, while putting into constant immersion time at 12 hours and concentration as indicated in Figure 5. It was observed that inhibitor efficiency (IE) decreased with a rise in temperature and the best inhibitor efficiency obtained at a temperature of 25 °C. The reduction in IE may be as a result of desorption at higher temperatures of the molecules of inhibitors from the surface of the metal [24-25]. Corrosion rate (CR) rises as temperature rose which is as a result of desorption of bio-molecules of MPL extract from the surface of the metal, resulting in greater portions of the surface of the metal being exposed to acidic medium. An increase in temperature also brings about increase in weight loss and increase in corrosion rate, CR [24, 26]. When the inhibitor covers the surface of the metal, it hinders corrosion process to set in since the surface of the metal has been coated with the inhibitor. It takes time for the inhibition coating to wear off and consequently, this slows down corrosion [27]. But when tem-



Figure 5. Effect of Temperature

perature increases, it causes the inhibitor to desorb from the surface of the metal thereby, causing a sharp rise in corrosion rate, and resulting in the decrease of the inhibitory efficiency. The reduction in the physical adsorption at higher temperature agrees that inhibition on the metal surface is physical in nature. Table 3 shows that the MPL compete favorably well with other plant extracts in literature.

3.6. Thermodynamic Study

Thermodynamic properties such as activation energy (E_a) , free energy change (ΔG) , entropy change (ΔS) and enthalpy change (ΔH) were estimated to further examine the impact of temperature on the inhibitory efficiency of the inhibitor. The Arrhenius equation was used to estimate the activation energy:

$$logCR = logA - \frac{E_a}{2.303R} \cdot \frac{1}{T}$$
(6)

Such that *CR* denotes corrosion rate, the activation energy is given as E_a , the molar gas constant is represented as *R* and *T* stands for temperature. Then, the slope of the graph of *logCR* against 1/T is shown in Figure 6 from where the activation energy was determined as presented in Table 4. The activation energy determined is 0.014 kJ/mol/K. All chemical reactions need a minimum amount of energy for the reaction to proceed which is known as activation energy. Low activation energy implies that the reaction is likely to occur spontaneously or without the intervention of catalyst or increase in temperature and thus favours the inhibition process. The ΔH and ΔS estimated are listed in presented in Table 4 using the slope and intercept of equation 7.

$$ln(\frac{CR}{T}) = ln(\frac{R}{Nh}) + \frac{\Delta S^{\theta}}{R} - \frac{\Delta H^{\theta}}{RT}$$
(7)

Such that h is the Planck's constant, Avogadro's number is given as N, R, T and CR are as previously defined above. The free energy change is concerned with how feasible and spontaneously a reaction will occur and this was obtained using equation 3 below:

$$\Delta G = -RT \ln(55.5K) \tag{8}$$

Table 3.	Com	parative	inhibition	efficiencies	as reported	in lit	terature with	1 MLP
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Plants	Inhibition Efficiency (%)	References
Neem ark extract	91.73	Desai [28]
Leaves extract of	97	Abiola et al. [29]
Gossipium		
Seed extract of	94	Abiola <i>et al.</i> [29]
Gossipium		
Khillah seed	71	El-Etre [30]
(Ammi visnaga)		
Justicia gendarussa	93	Satapathy et al. [31]
Pennyroyal oil	80	Bouyanzer et al. [32]
Occidimum	69	Oguzie [33]
Leaves of ankado	90.09	Desai [34]
ark extract		
Adathoda vasica	98.1	Shyamala and
		Kasthuri [35]
Eclipta alba	99.6	Shyamala and
		Kasthuri [35]
Centella asiatica	85	Shyamala and
		Kasthuri [35]
Bitter leaf	90	Caroline et al. [36]
root extract		
Cassia italica	87.4	Al-Otaibi et al. [37]
Tripleurospermum	83.4	Al-Otaibi et al. [37]
auriculatum		
Artemisia sieberi	86.2	Al-Otaibi et al. [3]
Gentian olivieri extract	93	Evrim <i>et al.</i> [38]
extract		
Musa paradisiacal	99.3	Present study
leave extract		



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Figure 6. A plot to determine Activation Energy



Figure 7. A plot to determine entropy and enthalpy

and K was estimated as:

$$K = \frac{\theta}{C(1-\theta)}.$$
(9)

All the parameters in equation 9 above are as previously defined above. A negative value of ΔG was obtained, showing that it is a spontaneous reaction. This is also used to determine the pathway of the experiment to either be physical adsorption or chemisorption. If ΔG is negative, then the process is more of physical adsorption, while a positive value of ΔG or relatively higher is chemisorption [39]. From this study, value of ΔG from the study of MPL extract inhibit on mild steel ranges between -5.57 and -4.96 kJmol⁻¹ which further indicate that the reaction pathway of corrosion is somewhat physical adsorption. Since Van der Waal force is responsible for adsorption, the process happens spontaneously i.e. it requires no activation energy. Enthalpy, on the other hand is seen to be positive, depicting an endothermic reaction. Corrosion is known to be exothermic reaction, because it increases with increase in temperature and this temperature comes from the surrounding. The value of enthalpy obtained from this study is $6.72 \ kJmol^{-1}K^{-1}$. This indicates that the inhibition process of the metal surface by the inhibitor (MPL) is endothermic in nature. It has been noted from

experiment that positive enthalpy (endothermic) value and low entropy (-) is best for inhibition which is in line with what was observed in this study and that a rise in temperature reduces inhibition and increase the corrosion rate [27]. Entropy depicts the degree of disorderliness of a slope and this is brought about by high temperature that causes the molecule to move randomly due to gained energy which explains desorbing of the MPL extract from the surface of the metal and this will leads to low inhibitor efficiency. Thus, a relatively low temperature is required for an effective and efficient inhibition process. So, for corrosion process, it always leads to the evolution of heat, while for the adsorption of inhibitor onto the metal surface, the process is always endothermic because higher temperature will results in desorption of the inhibitor from the surface. So, while corrosion is favoured by exothermic process, inhibition process (adsorption on metal surface) is favoured by endothermic process.

3.7. Inhibitor Mechanism

It is important to note that steel is an alloy of carbon and iron where the carbon atom is bonded to iron to reduce corrosion and the formation of steel is a function of Fe - C phase present i.e., Ferrite (αFe), Austenite (γFe), Cementite (Fe_3C),

Table 4. Thermodynamic properties of Musa paradisiacal						
Temperature	$\Delta \mathbf{G}$	$\Delta \mathbf{H}$	$\Delta \mathbf{S}$	E_a		
(K)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)		
298	-5.57					
308	-5.10	6.72	-197.53	0.014		
318	-4.99					
333	-4.96					

Pearlite ($\alpha Fe+Fe_3C$) [40]. The bonding of *C* with *Fe* in Cementite made the $3d^6$ electrons of *Fe* to remain in t_{2g} that is low spin [41]. Consequently, the four electrons of the carbon are made readily available to the e_g -orbital for bonding. The ferrite regions are the most reactive site and tend to corrode easily [42]. The iron particles become oxidized in water when they are lost to the water's acidic electrolytes, resulting in the formation of Fe^{2+} . The formed *Fe* ion at the anode migrates to the cathode. The hydroxyl ions formed from reaction of the hydrogen ion produced with oxygen react with Fe^+ to produce hydrous iron oxide (FeOH), also which is often called rust [43].

When inhibitors are added into corrosive medium in minute quantity, they retard the corrosion process. The inhibition of corrosion process is successful when Fe^{2+} is stabilized from further oxidation to Fe^{3+} . Either physical adsorption or chemisorption is the process through which inhibitors should readily be adsorbed to the metal surface so as to be an effective shield opposing the metal corrosion [44]. The inhibitor group's physicochemical properties, like the functional group, the donor atom electronic density and molecular structure depend primarily on one of these adsorption processes. Corrosion inhibition mechanism is also accomplished in aromatic rings, nitrogen and oxygen containing molecules which donate their lone pair of electrons to the metal and thus favoring the uptake of these molecules onto the surface of the metal [45]. Furthermore, molecules having large structure occupy a larger surface area and thus developing a protective coating. Plantain leaves on this note have inhibitive properties as they have been identified by GC-MS analysis to contain compounds such as 6-Amino-1,3,5-triazine-2,4(1H,3H)- dione, 9-Octadecenamide, (Z)- Ole amide, Polygalitol, Cyclotetrasiloxane, octamethyl-, Thiophene, 2,3-dihydroand Ginsenol which contain elements such as O, N or S which serves as electrons donors. These molecules of inhibitors contain strong ligands such as CN^- , NH^3_- , OCN^- , SCN^- , etc, which causes low spin forcing the $3d^6$ electrons into t_{2g} orbital (dxy, dxz and dyz). The degree of splitting is the inverse of the strength of ligands. This disrupts the degeneracy and increasing the energy of the e_g orbital which allows for the donating of electron by the ligand to the empty e_g orbital $(dx^2 - y^2)$ and dz^2) [46]. When this donated electron by the inhibitor molecules or ions (ligand) is dative covalent bond between the inhibitor and metal, weak bond or Van der Waal force of attraction is produced, which is physical adsorption (physical adsorption). While an ionic bonding gives rise to chemisorption due to strong electrostatic bond created [47].



Figure 8. Fe^{2+} ion and Energy levels of d orbital in octahedral field (Low spin)



Figure 9. Isotherm plot of Langmuir isotherm

3.8. Isotherms Study

Adsorption isotherm can reveal information relating to the adsorption mechanism, surface coverage, and adsorption equilibrium constant. To verify the isotherm, the linear relation that exists between θ and *C* was established using the value of the correlation coefficients (R^2) of Langmuir isotherm as illustrated in equation 10:

$$\log\frac{C}{\theta} = \log C - \log b,\tag{10}$$

where *b* stands for inhibitor adsorption equilibrium constant. Figure 9 depicts the plots of $logC/\theta$ against the inhibitor concentrations (*C*) at 303 *K*. From the calculated value of correlation coefficients (R^2) which is 0.971, it can be said that the Langmuir isotherm can also be deployed to explain the inhibition process which assumed a physical reaction with weak intermolecular forces.

4. Conclusion

This work examined the potency of leaf extract of *Musa* paradisiaca (MP) as inhibitor against the corrosion of mild steel

in acidic medium. An immersion period of 12 hours was perceived as the best performance for MPL for the whole concentration of the inhibitor examined. Inhibitor efficiency (IE) reduced with rise in temperature. The reduction in I.E. is as a result of desorption of the molecule of the inhibitor at higher temperatures from the surface of the metal. The reaction at the surface of the metal by the extract is endothermic with the positive enthalpy obtained from this study as 6.72 kJ/mol/K, suggesting a mix adsorption process but having chemical adsorption predominate on the surface of the metal. The value of ΔG obtained from the study of MPL extract inhibit on mild steel in *HCl* ranges between -5.57 and -4.96 $kJmol^{-1}$ which further indicated that the reaction pathway is achieved by adsorption on the surface at the studied temperatures. From the experimental result gathered, it can be concluded that the plant leaf extract of MP inhibitor extracted is efficient in inhibiting steel.

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