

# Green Approach to Corrosion Mitigation: A Study on the Inhibitive Effects of *Parquetinanigrescens* Extract

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## Abstract

The mitigation of the corrosion of mild steel by ethanolic extract of *Parquetina nigrescens* (EEP<sub>N</sub>) in 1 M HCl was explored using the weight-loss method. The inhibition efficiency (I.E) of the extracts varied with the concentration of extracts, time of immersion and temperature. The results obtained shows that as the concentration of the extract increase, the corrosion rate decreased. The I.E increases with an increase in the concentration of the extract. The temperature effect on the I.E of EEP<sub>N</sub> revealed that as the temperature increases, inhibition efficiency increases. The enthalpy ( $\Delta H^\circ$ ) positive values in the uninhibited and inhibited of the EEP<sub>N</sub> are endothermic in nature. The negative free energy for EEP<sub>N</sub> suggests the spontaneity and feasibility of the reaction. Langmuir gives the best fit with  $R^2$  value of 0.9999, very close to unity. The Fourier transform infrared spectroscopy and surface morphology of the extract's constituent on the surface of the mild steel established the effectiveness of the inhibitive effect of the extract. Potassium iodide enhances in increasing the value obtained for the I.E and decrease in the rate of corrosion. The EEP<sub>N</sub> acts as a good inhibitor for the corrosion of mild steel in acidic medium.

**Keywords:** corrosion inhibition, *parquetina nigrescens*, thermodynamics, kinetics, potassium iodide

## 1. Introduction

The breakdown of metal due to chemical or electrochemical reactions is referred to as corrosion. Corrosion usually occurs as a result of oxidation with air molecules in the presence of water. Mild steel has been the most widely used alloy for both structural and industrial applications from the time when industrial revolution started [1]. The invention of new large-scale steel resulted from the fast development in the manufacturing, automotive, and textile industries [1]. One of the industries' challenges is the mild steel decomposition due to the exposure of these materials to a corrosive medium, salt solutions, and alkalis [2]. Various researches have been carried out on how to mitigate the corrosion of metals and their alloys [2, 3]. One of the most methods for mitigating the mild steel corrosion in a corrosive medium is the use of inhibitors. Various numbers of organic and inorganic inhibitors have been used to prevent corrosion which showed good anti-corrosive activity, but they are not without a fault. Most of these compounds are toxic to humans and its environs, maybe during the synthesis of the compound or when applied. This can damage the organs such as liver/kidney or interrupt a biological process [4]. Though the compounds having  $\pi$  bonds are said to be the effective and efficient, but the biological toxicity of the materials are attested for its environmental harmful features [5]. Organic inhibitors mitigate corrosion by adsorption process; thus, when the inhibitors are adsorbed on the metal surface it prevents the dissolution reaction of metal in a corrosive environment [6]. Because of their shortcomings, their uses in the mitigation of corrosion are limited. The natural plant extracts have gained much importance in inhibiting mild steel corrosion because it's cheap, biodegradable, readily available, eco-friendly, and more efficient and renewable source of materials [6- 9]. The corrosion mitigation of mild steel in acidic solution using natural plant extracts has been previously reported. Bochuan et al. proposed the study of papaya leaves extract as a novel eco-friendly corrosion inhibitor for Cu in H<sub>2</sub>SO<sub>4</sub> medium [9]. Irfan et al. investigate and evaluate neem leaves extract as a green inhibitor for corrosion behavior of mild steel [10]. Alaneme et al. have contributed to the corrosion of inhibition in acidic solutions using *Hunteria umbellata* seed husk extract [11]. Manimegalai et al. studied the corrosion inhibition of mild steel in aqueous media using *Sargassum swartzii* (Brown algae) [12]. Akinbulumo et al. investigated the corrosion inhibition of mild steel using *Euphorbia heterophylla* L. extract [6]. The research works cited above motivated the study of *Parquetinanigrescens* leaves as a novel ecofriendly corrosion inhibitor to mitigate the corrosion of mild steel in 1 M HCl. *Parquetinanigrescens* is an

herbaceous and of the Asclepiadaceae family. It is woody at the base and measures between 7-8m in length. The plant is normally found growing in African and South America. *Parquetina nigrescens* has been found to contain tannins, phlobatannins, saponins, cardiac glycosides, cardenolides, ascorbic acid, alkaloids, steroids, phenolics, anthraquinones and triterpenes [13- 15]. These components fascinated our attention towards corrosion studies, using this plant extract. *Parquetina nigrescens* have been reported to have antioxidant and antimicrobial properties used for wounds in African and have sympathomimetic effects [14]. It also stimulates increased uterine contraction due to the mobilization of extracellular calcium like oxytocin impact [16]. This investigation aims to examine the effect of ethanolic extract of *Parquetina nigrescens* (EEN) as a novel green and natural material on corrosion inhibition of mild steel in 1 M HCl solution by weight-loss measurement. Scanning electron microscopy and Fourier transform Infrared spectroscopy were used to characterize the products. The kinetic of corrosion was described using thermodynamics parameters and the adsorption process when varying concentration and temperature of EEN.

## 2. Material and methods

The composition of the mild steel coupon used is 98.98% Fe, 0.21% C, 0.25% Si, 0.46% Mn, 0.0090% S, 0.0110% Ni, and 0.0090% P. The sheet was pressed mechanically, cut to sizable forms of specimen, each of dimensions 5 X 20mm. Each coupon was cleaned using ethanol, dried and kept in a desiccator. All the chemicals used for the experiment were analytical grade and double-distilled water was used to prepare the solutions.

### 2.1 Stock solution of *Parquetina nigrescens* leave

The leaves were collected at North gate, Federal University of Technology, Akure. The leaves were sun-dried, grounded and sieved through a mesh 850-micron sieve. It was later soaked in ethanol solution for 72 h. The leaves were filtered and then the ethanol was allowed to evaporate after 72 h. The working solutions were diluted to obtain desired concentrations from the stock solutions prepared.

### 2.2 Gravimetric study

The weight loss experiment was conducted by dipping the pre-cleaned mild steel coupons in 100 ml of HCl solution with or without inhibition, tested at 303 and 333 K and maintained in a thermostated water bath. The weight-loss was made by recovering the samples after 2 h of immersion. After 2 h, each of the samples was retrieved from the solution, washed with double distilled water and acetone and allowed to dry. The weight difference was used as the mild steel weight-loss. The obtained weight loss, inhibition efficiency of the extract, corrosion rate, and surface coverage of mild steel were calculated using equations 1, 2, and 3 respectively.

$$IE\% = \frac{W_o - W_i}{W_o} \times 100 \quad (1)$$

where  $W_o$  and  $W_i$  = weight-loss values in the uninhibited and inhibited

$$CR = \frac{W}{AT} \quad (2)$$

where  $W$  = weight-loss in g,  $A$  = mild steel area and the  $T$  = immersion period

$$\text{Surface coverage } \theta = 1 - \frac{W_o}{W_i} \quad (3)$$

where  $W_o$  and  $W_i$  = weight-loss values in the uninhibited and inhibited

### 2.3 Scanning electron microscopy analysis

The mild steel samples were dipped in 1 M HCl solution for 2 h in 1% EEN. The samples were retrieved and dried after 2 h. The mild steel surface morphology was studied by scanning electron microscopy (SEM, ZEISS Ultra PLUS).

### 2.4 Fourier transform infrared spectroscopy analysis

Fourier transform infrared spectroscopy (FTIR) analysis of EEN and the inhibited dried mild steel powder were examined using Perkin-Elmer-1600 Fourier transform infrared spectrophotometer. The inhibitor (1% EEN) was

molded to form a protective film on the mild steel surface in 1 M HCl for 2 h. The samples were recovered and dried after 2 h. FTIR spectroscopy was used to examine the film between the interfaces of the metal solution.

### 3. Results and discussion

#### 3.1 Effect of concentration on corrosion rate

The mild steel corrosion rate in the uninhibited and inhibited EEPN at various concentrations is shown in Figure 1. The result showed that as the concentration increases, the mild steel corrosion rate in 1 M HCl decreased. This implies that adding EEPN to the medium led to a significant decrease in the mild steel corrosion rate and decreased as the concentration of the extract increases as reported by Olasehinde *et al.* [17]. As the temperature increased, corrosion rate decreased. This could be as a result of the increase in the average kinetic energy as the molecules react. The result gotten for the corrosion rate agrees with that described by Akinbulumo *et al.*, and Olasehinde *et al.*, [6, 17] in which the decreased corrosion rate increased with temperature.

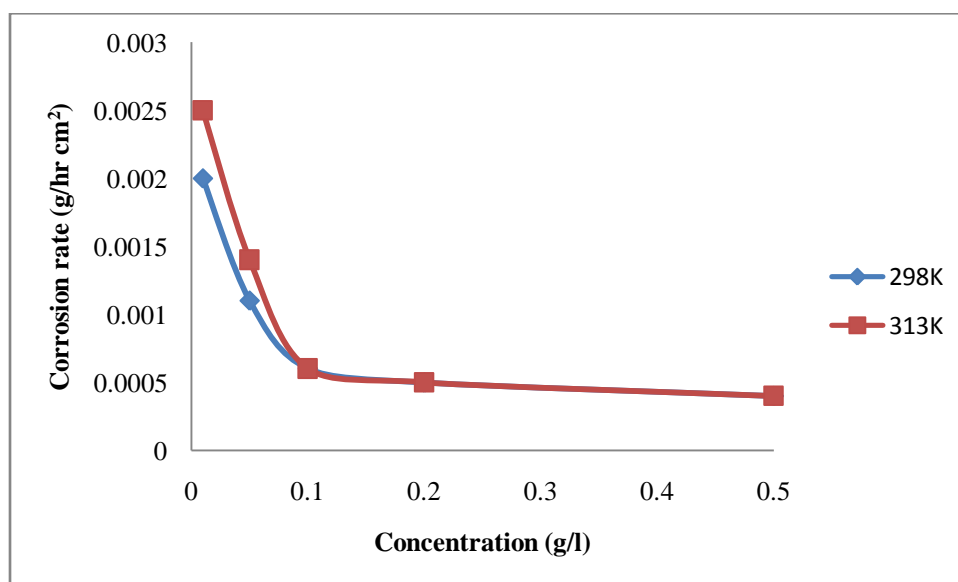


Figure 1 Concentration effect of EEPN on mild steel corrosion rate in 1M HCl

#### 3.2 Concentration effect on inhibition efficiency

To study the concentration effect on corrosion inhibition efficiency (I.E), the mild steel specimen was dipped in 1 M HCl of various concentrations of EEPN at a temperature of 298 and 313 K. The I.E of various concentrations of EEPN is presented in Figure 2. The plot showed that the I.E increased with an increase in concentrations of EEPN attaining a maximum value of 90.48% at the temperature of 313 K. The increase in the I.E value as the temperature increased could be due to the uptake of some additional chemical molecules. The result proposes that there might be chemical bonding between the mild steel surface and the EEPN [4]. This established that EEPN forms a protecting film on the surface of the mild steel even at high temperature.

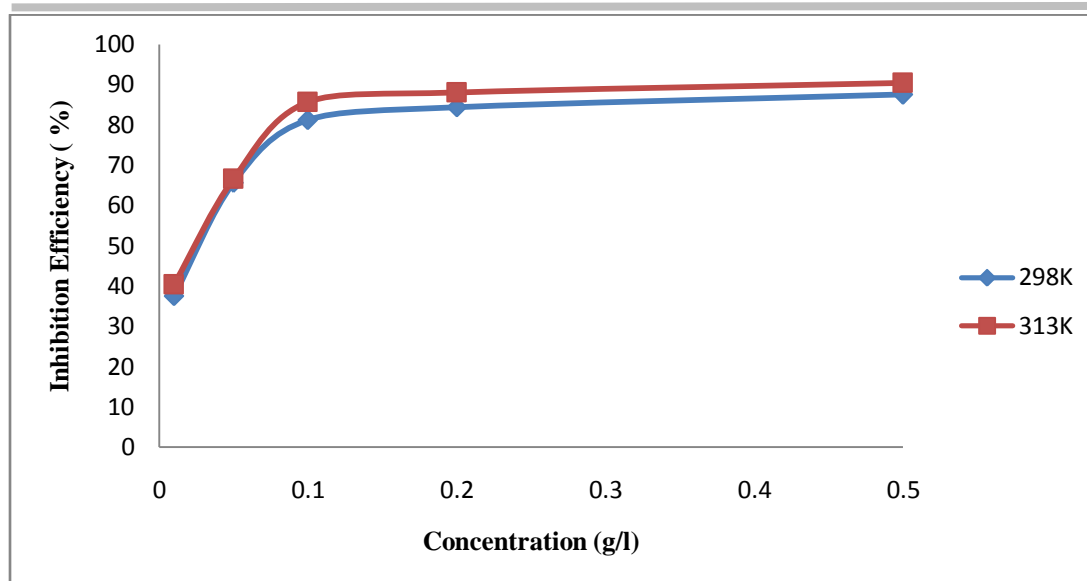


Figure 2 Concentration effect of EEPN on the I.E of mild steel

### 3.3 Temperature effect on corrosion rate

The temperature effect on the mild steel corrosion rate in the uninhibited and inhibited of various concentrations of EEPN was done by varying the temperature from 303 to 333K, as presented in Figure 3. The result obtained shows that as the inhibitor increases with an increase in temperature, the rate of corrosion decreased. This shows the plant extract's effectiveness in mitigating or causing a barrier between the acid and the mild steel. This occurs because the increase in temperature increases the reacting molecules' average kinetic energy, increasing the reaction rate. The decrease in corrosion rate results from the inhibiting effect of EEPN, thereby mitigating the corrosion on mild steel [9].

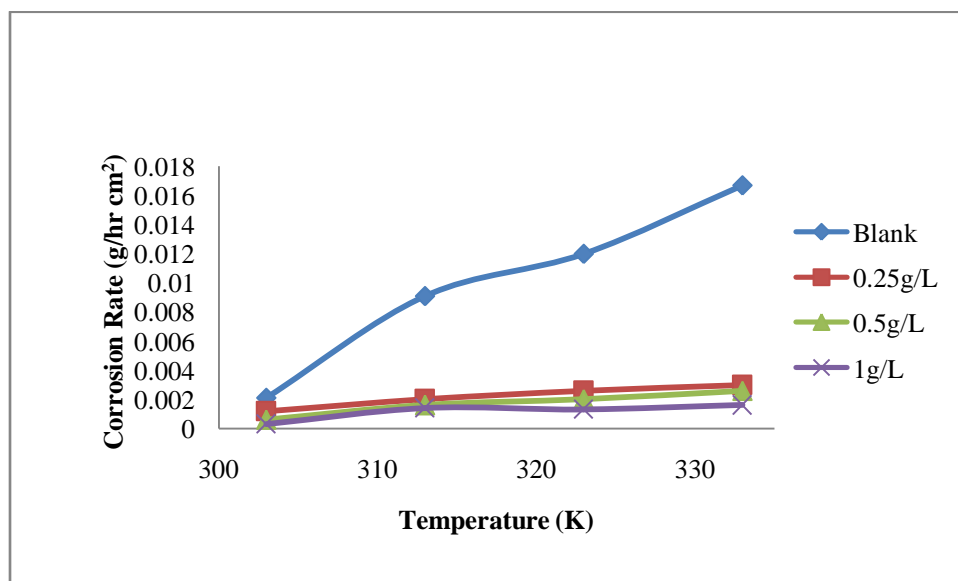


Figure 3 Temperature effect of EEPN on mild steel corrosion rate

### 3.4 Temperature effect on inhibition efficiency

To study the temperature effect on corrosion inhibition efficiency, the mild steel samples were dipped in 1 M HCl having different concentrations of EEPN at different temperature range, 303- 333 K. The influence of temperature on

the inhibition efficiency of EEPN in 1 M HCl is shown in Figure 4. The result shows that the inhibition efficiency increased with an increase in temperature at different concentrations as the concentration of the inhibitor increases. The increase in inhibition efficiency due to the temperature rise indicates that the uptake of EEPN molecules occurs on the mild steel surface and equilibrium takes place between two processes at a certain temperature [18,19]. This reveals that EEPN is a promising inhibitor for mitigating decomposition of mild steel.

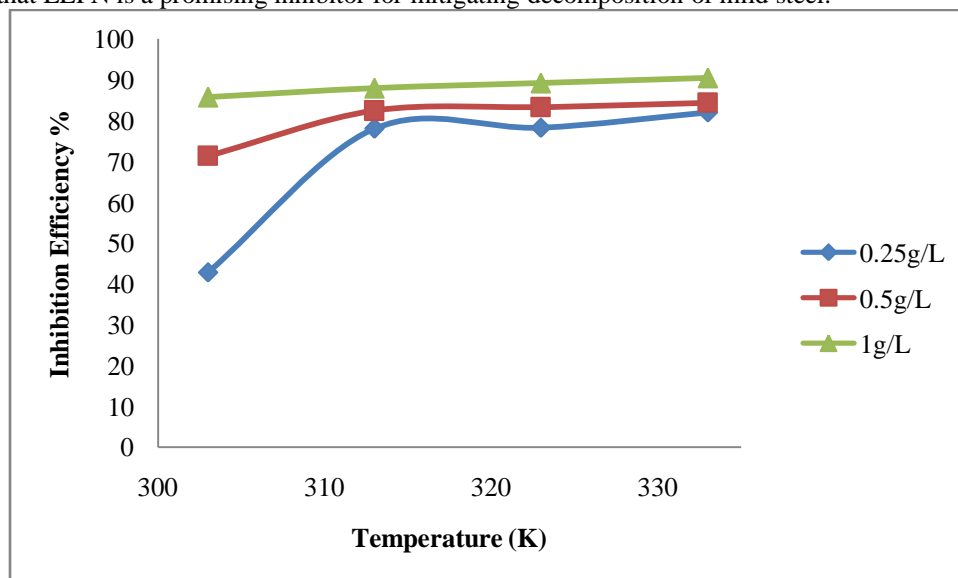


Figure 4 Temperature effect of EEPN on the inhibition efficiency of mild steel

### 3.5 Adsorption isotherm study

The adsorption isotherms are used to explore the method of uptake and the characteristic of adsorption of inhibitor on the surface of the mild steel. The metal's nature/charge influences adsorption, chemical structure, electrolyte type, and distribution charge in the molecule [20, 21]. The degree of surface coverage ( $\theta$ ) is very significant in adsorption isotherms. The value of  $\theta$  for various concentrations of EEPN from the weight-loss dimensions was gotten via  $\theta = I\%/100$ . The correlation between inhibition efficiency and surface coverage was fitted into three adsorption isotherms namely: Langmuir, Temkin and Freundlich. The correlation coefficients ( $R^2$ ) were used to determine the best-fitted isotherm. These isotherms are described in equation 4:

$$F(\theta, x) \exp(-2a\theta) = KC \quad (4)$$

Where  $f(\theta, x)$  = configurational factor which depends on the physical model and theory underlying the derivative of the isotherm,  $\theta$  = surface coverage,  $C$  = concentration inhibitor,  $x$  = size ratio,  $a$  = molecular interface parameter,  $K$  = equilibrium constant of the adsorption process.

The surface coverage helps to describe the isotherm that best fit to define the adsorption process. The adsorption experimental data fit into Langmuir, Temkin, and Freundlich adsorption isotherm (Figure 5-7) but Langmuir adsorption isotherm gives the best fit. Langmuir isotherm with  $R^2$  values of 0.9999 very near to unity, best describes EEPN adsorption mechanism on mild steel in 1 M HCl acid medium. Hence, Langmuir adsorption isotherm is used for estimating the adsorption equilibrium constant ( $K_{ads}$ ) and can be expressed using this equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

where  $C$  = inhibitor concentration,  $K_{ads}$  = sorption stability constant, and  $\theta$  = degree of surface coverage calculated using weight loss values at 303-333 K in 1 M HCl using various extract's concentrations. The  $C/\theta$  values were plotted against  $C$  as presented in Figure 5. The values of  $K_{ads}$  are related to  $\Delta G_{ads}^0$  using equation 6:

$$\Delta G_{ads}^0 = -RT \ln(55.5 \times K_{ads}) \quad (6)$$

where  $R$  = gas constant,  $T$  = Absolute temperature, the value of  $55.5$  = molar concentration of water in medium expressed in  $\text{mol}^{-1}$  concentration. The thermodynamics sorption parameters are shown in Table 1. The  $\Delta G^{\circ}_{\text{ads}}$  values are negative and less than  $20 \text{ kJ/mol}$  (Table 1). This result shows that the EEPN sorption on the mild steel surface is feasible, spontaneous, and follows the mechanism of physical adsorption. The values of  $\Delta G^{\circ}_{\text{ads}}$  around  $-20 \text{ kJ/mol}$  or lower indicate physisorption, while those higher than  $-40 \text{ kJ/mol}$  indicate chemisorption. In this study, physical sorption shows electrostatic attraction between the charged species in the medium and the charged metal surface.

Table 1 Thermodynamic parameters for sorption of EEPN on the mild steel in 1M HCl

Temperature (K)	$K_{\text{ads}}$	$\Delta G^{\circ}$ (kJ/mol)	$R^2$ (Langmuir)	$R^2$ (Temkin)	$R^2$ (Freundlich)
303	2.8577	-12.762	0.9897	0.9819	0.9645
313	23.9517	-13.183	0.9999	0.9977	0.9967
323	17.1092	-13.604	0.9998	0.9990	0.9996
333	20.8952	-14.025	0.9995	0.9705	0.9731

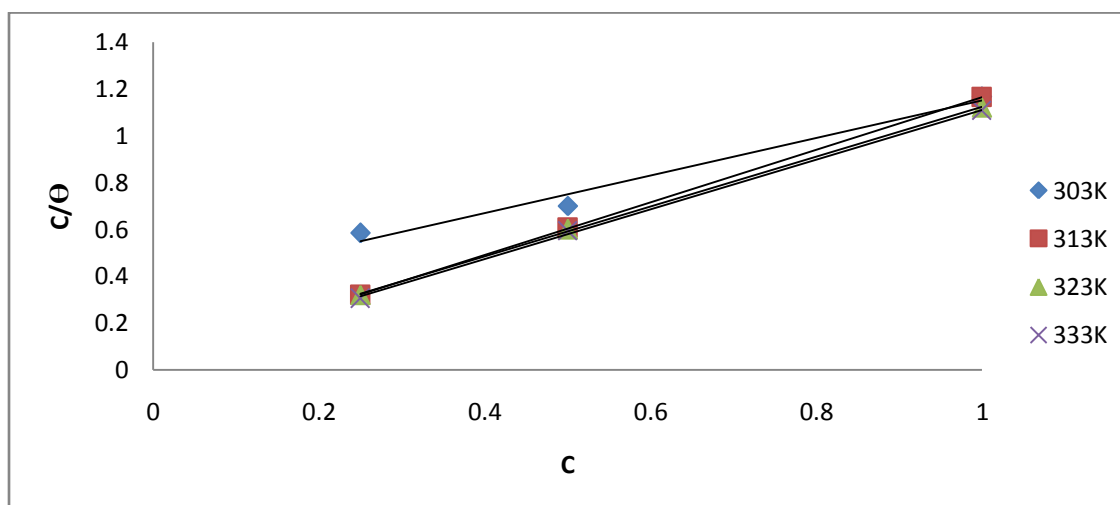


Figure 5 Langmuir adsorption isotherm for the EEPN in 1 M HCl

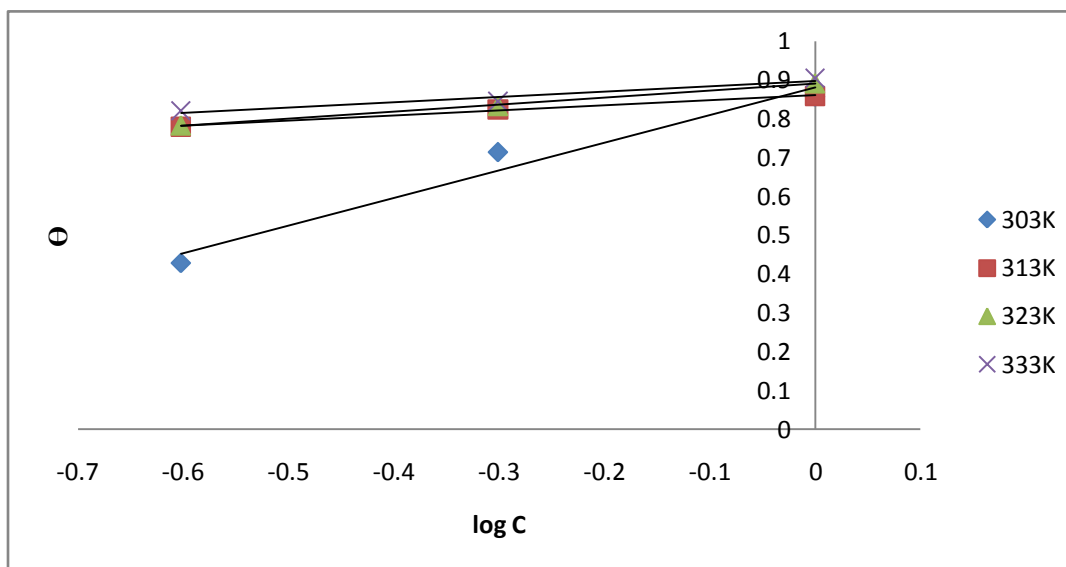


Figure 6 Temkin adsorption isotherm for the EEPN in 1 M HCl

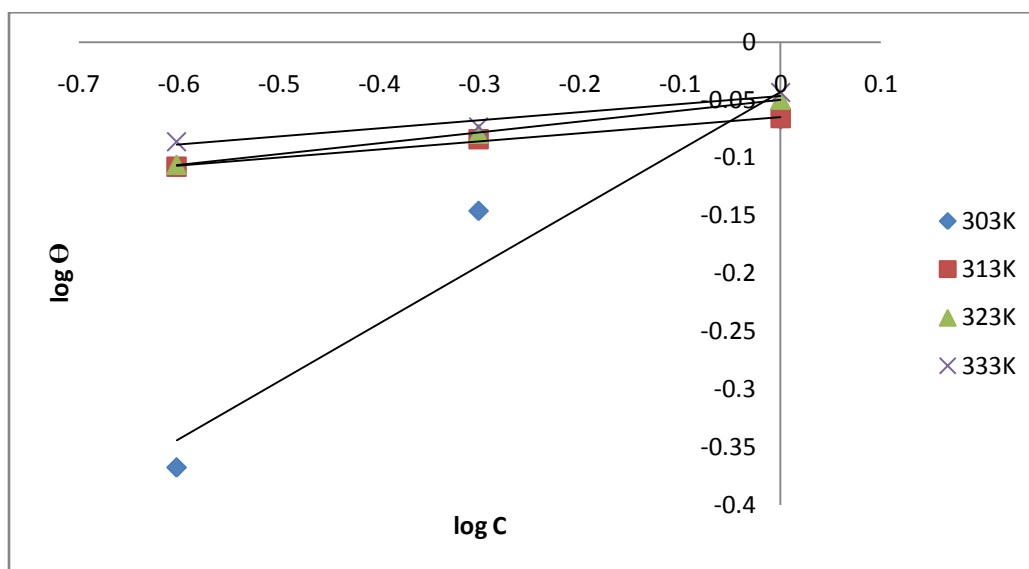


Figure 7 Freundlich adsorption isotherm for the EEPN in 1M HCl

### 3.6 Determination of Activation energy

In the study of metal dissolution, temperature plays an important role. Some changes could occur on the mild steel surface due to the temperature effect on the inhibited acid metal reaction, such as the inhibitor's desorption. The inhibitor may experience dissolution or quick etching. The temperature effect on the rate of corrosion and inhibition process was done using weight-loss study by varying the temperature from 30- 60°C in 1 M HCl in the uninhibited and inhibited of various concentrations (0.25-1 g/L) of EEPN. The rate of corrosion in the uninhibited and inhibited extract increase with a temperature rise after 2 h of immersion. The I.E. increases as the temperature increases for the various concentrations of the extract.

The dependency of rate of corrosion on temperature can be stated through the Arrhenius equation

$$\log CR = \log \lambda - \frac{E_a}{2.303 RT} \quad (7)$$

where CR= corrosion rate,  $E_a$ = apparent activation energy,  $\lambda$ = frequency factor, T= absolute temperature, and R= molar gas constant. Figure 8 shows a plot logarithm of CR versus  $1/T$  for *Parquetin nigrescens* in 1M HCl solution both in the uninhibited and inhibited extract concentrations. This gives a straight line with a coefficient regression near unity.

From the slopes of the linear plots, the  $E_a$  values were deduced and are stated in Table 2. The value of  $E_a$  in the inhibited may be equal, lower or higher than those in the uninhibited [1]. The  $E_a$ 's value is lower in the inhibited solution of various concentrations of the EEPN than for the uninhibited solution due to the inhibitor's adsorption molecules on the metal surface [1]. The decrease in the activation energy of the inhibitor signifies chemisorption while the inverse can be attributed to physisorption. This conclusion symbolized that as the temperature increases, inhibition efficiency increases. This shows that EEPN mitigates the decomposition of mild steel in the acid solution. A related outcome has been described by Karthik *et al.*, [4] on the mitigation of corrosion of carbon steel using *Tiliacora acuminate* leaves. The increase in  $E_a$  is related to the concentration of the extract, which can be inferred as physical adsorption, indicating that the corrosion processes' energy barrier also increases.

Table 2 Values of activation energy with the different concentration of the extract

Conc. of the extract	$E_a$ (kJ/mol)	$\Delta S$ (J/mol/K)	$\Delta H$ (kJ/mol)
Blank	55.29	-120.096	52.6510
0.25	25.44	-225.113	22.8051
0.5	39.27	-184.325	36.6350
1.0	42.54	-177.652	39.9062

The enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of activation of corrosion process were calculated from the equation:

$$CR = \left(\frac{RT}{nh}\right) \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(\frac{\Delta H^\circ}{RT}\right) \quad (8)$$

where  $R$ = universal gas constant,  $T$ = absolute temperature,  $n$ = Avogadro's number,  $h$ = Planck's constant,  $\Delta S^\circ$ = entropy of activation and  $\Delta H^\circ$ = enthalpy of activation. Figure 9 illustrates a plot of  $\text{Log}(CR/T)$  as a function of  $1/T$ . A linear plot with an intercept of  $(\ln R/nh + \Delta S^\circ/R)$  and a slope of  $(-\Delta H^\circ/R)$  was obtained. The estimated  $\Delta S^\circ$  and  $\Delta H^\circ$  values were estimated and shown in Table 2.

The result shown in Table 2 shows that the positive values of  $\Delta H^\circ$  is endothermic. The activation enthalpies differ similarly as the  $E_a$ , thereby supporting the suggested mechanism of inhibition. The entropies negative values suggest that the system exhibits random behavior. A related observation has been described in the literature [4, 22]. The  $\Delta S^\circ$  values were negative suggesting that the adsorption was enthalpy-driven due to the exothermic enthalpy of adsorption for the EEPN.

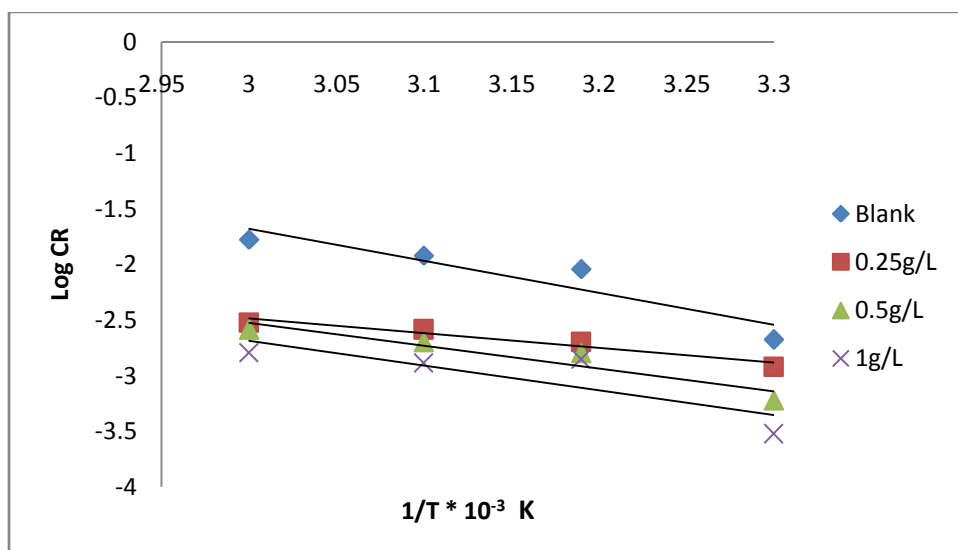


Figure 8 Arrhenius plot for corrosion of mild steel in 1M HCl in the uninhibited and inhibited various concentration of EEPN

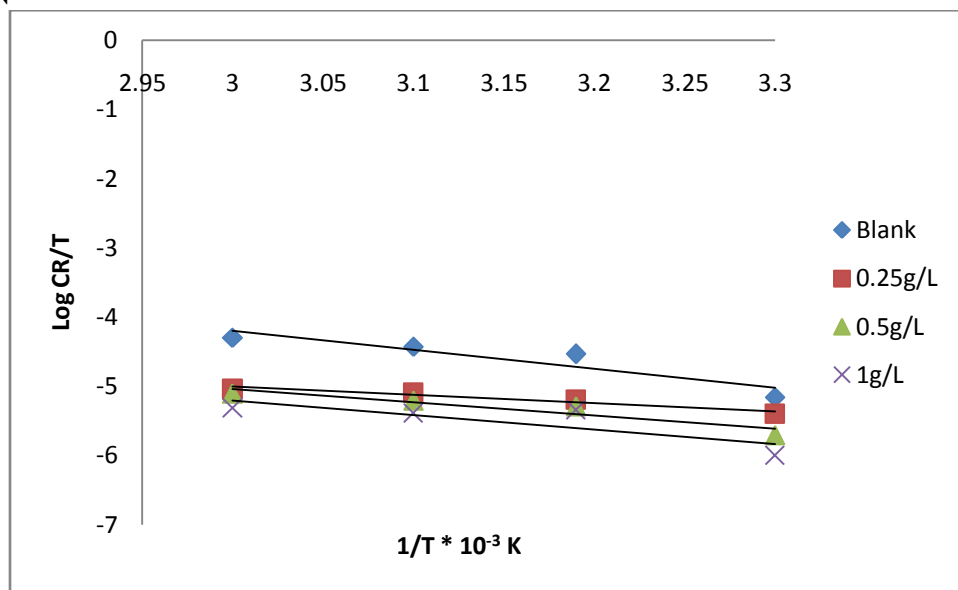


Figure 9 Transition state plot for corrosion of mild steel in 1 M HCl in the uninhibited and inhibited various concentration of EEPN



### 3.7 Kinetic study

#### 3.7.1 Rate constant and half-life determination

Corrosion process' kinetics procure the type of a diffusion process, where at high temperature, the amount of inhibitor at the surface of the metal is lower than at lower temperatures [23, 24]. The rate constants were calculated using equation 9:

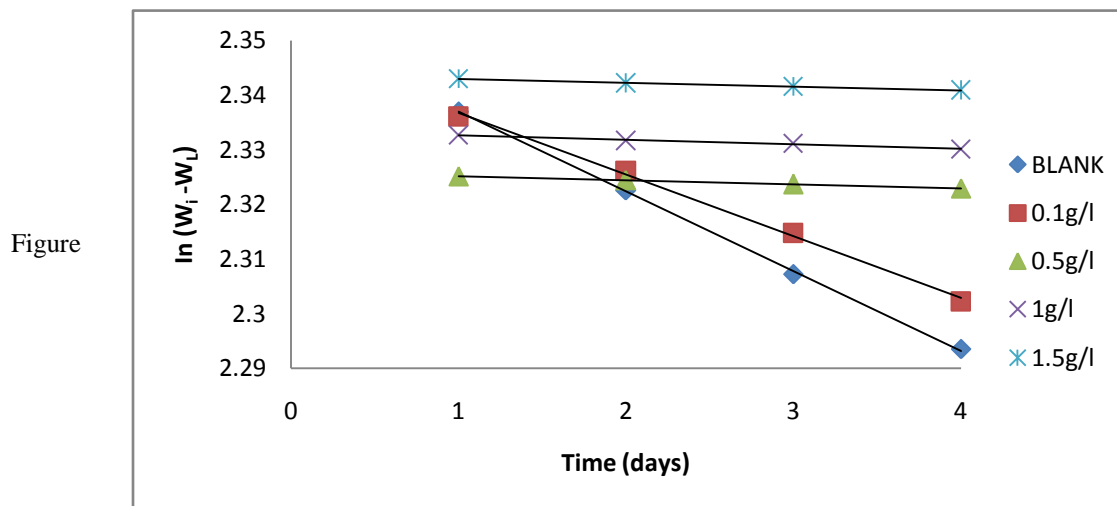
$$\ln (W_i - W_L) = -k_1 t + \ln W_L \quad (9)$$

The linear plots of  $\ln(W_i - W_L)$  against time at 30 °C was carried out. From the plot, a slope  $k_1$  confirmed a first-order kinetics reaction with reverence to the decomposition of mild steel in 1 M HCl solution in the EEPN (Figure 10).

The half-life ( $t_{1/2}$ ) was estimated using equation 10:

$$t_{1/2} = 0.693/k_1 \quad (10)$$

The increase in half-life ( $t_{1/2}$ ) as shown in Table 3 was due to *Parquetina nigrescens* extract presence confirming the mild steel inhibition in 1M HCl. The corrosion rate decreases as the half-life increases, signifying a decrease in the solutions' mild steel dissolution rate. Therefore, there is no doubt that the entire mild steel surface obtained a multilayer protecting coverage.



10Variant of  $\ln(W_i - W_L)$  with time for mild steel in 1M HCl medium in the presence of EEPN

Table 3 Rate constant and half-life parameters

Concentration of the extract	Rate constant $K \text{ (day}^{-1}) \times 10^{-3}$	Half-life ( $t_{1/2}$ ) (days)
Blank	0.0335	20.6280
0.1	0.0259	26.6838
0.5	0.0016	408.2839
1.0	0.0018	366.5136
1.5	0.0015	440.8256

#### 3.8 Effect of Potassium iodide on corrosion rate and inhibition efficiency

The potassium iodide on the corrosion rate and inhibition efficiency on *Parquetina nigrescens* is shown in Figure 11 and 12. It was observed that potassium iodide increases the value obtained for the inhibition efficiency and decrease in corrosion rate. The experiment was done for variation of potassium iodide molarity which ranges from 0.025-

0.075M for one concentration which is 0.5w/v. The result shows that as the molarity of potassium iodide increase, the corrosion rate decrease and the inhibition efficiency increases.

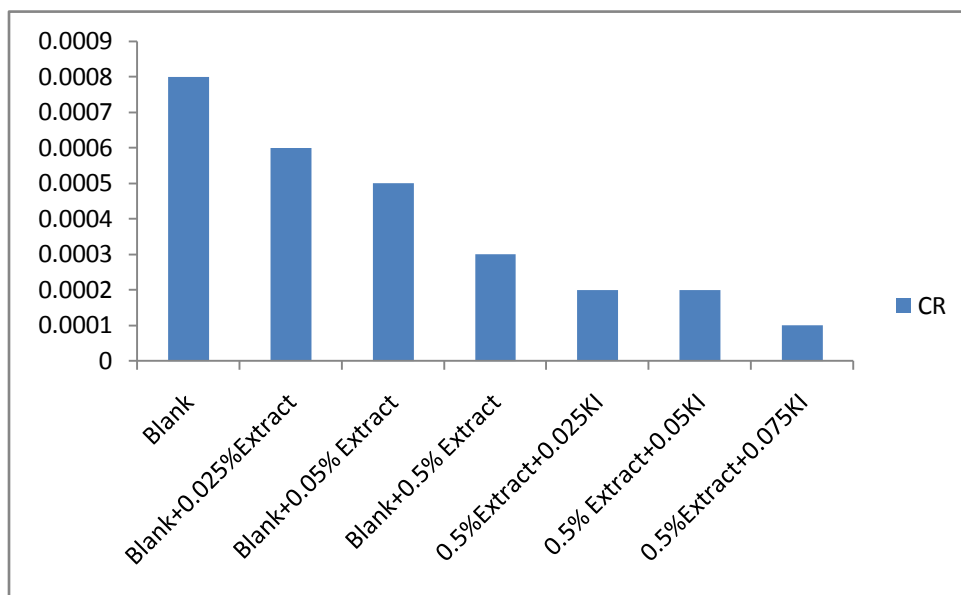


Figure 11 Potassium iodide effect on the corrosion rate of EEPN

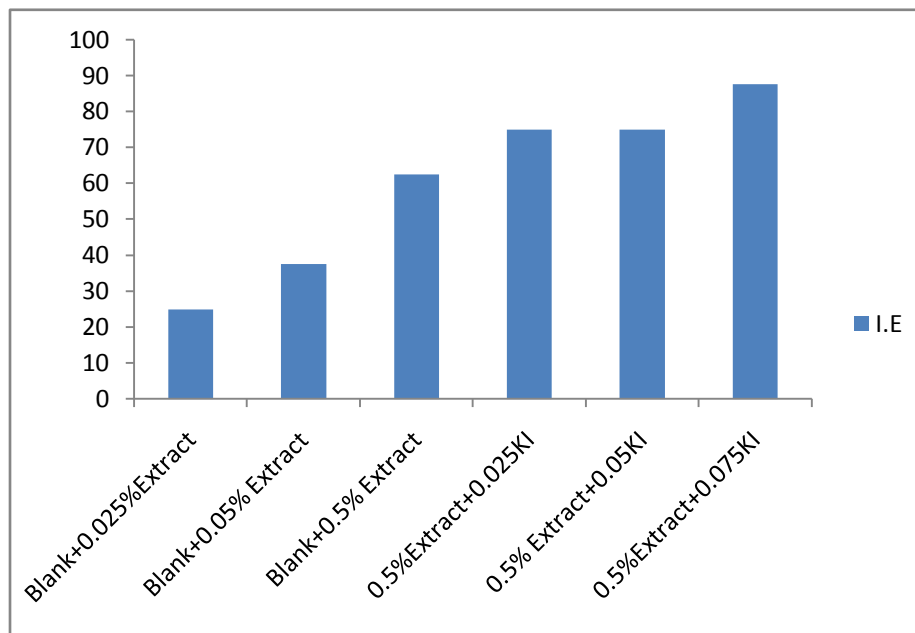


Figure 12 Potassium iodide effect on Inhibition efficiency of EEPN

### 3.9 Phytochemical analysis

The EEPN phytochemical analysis was done in accordance to the method stated by Onyeka and Nwabekwe [16]. Inspection of these phytochemical constituents' chemical structures shows that the compounds are hydrolyzable and the compounds can accumulate on the metal surface. This happens through the lone pair of electrons that are on their oxygen functional groups causing a barrier for mass transfer and charge, thereby decreasing the metal's interface with the corrosive medium. Thus, this led to a decrease in the rate of corrosion of the mild steel.

Table 4 Some phytochemical constituents of EEPN

Phytochemical constituents	Qualitative	Quantitative value (mg/g)
Steroid	-	-
Terpenoid	+	13.0855
Saponin	++	16.4550
Tannin	+	14.1155
Flavonoid	+	11.8165

### 3.10 SEM analysis

The mild steel surface morphology in 1M HCl solution in the uninhibited and inhibited EEPN is shown in Figure 13. The surface analysis using a SEM provides info on the degree of attack and the inhibition ability of EEPN on the mild steel surface. The rough surface obtained (Figure 13a) when the metal was dipped in 1 M HCl solution for 4 h without EEPN shows significant corrosion. Nevertheless, in Figure 13b, with the addition of EEPN, the surface improved noticeably in terms of smoothness, signifying a significant reduction in the corrosion rate. This implies that EEPN could form a protective film on the mild steel surface, thus reducing the metal disintegration in acidic solution. The inhibitor prevents a direct and intensive attack on the metal. The surface morphology of the protective film adsorbed on the mild steel surface established a great performance of the inhibitive effect of the extract.

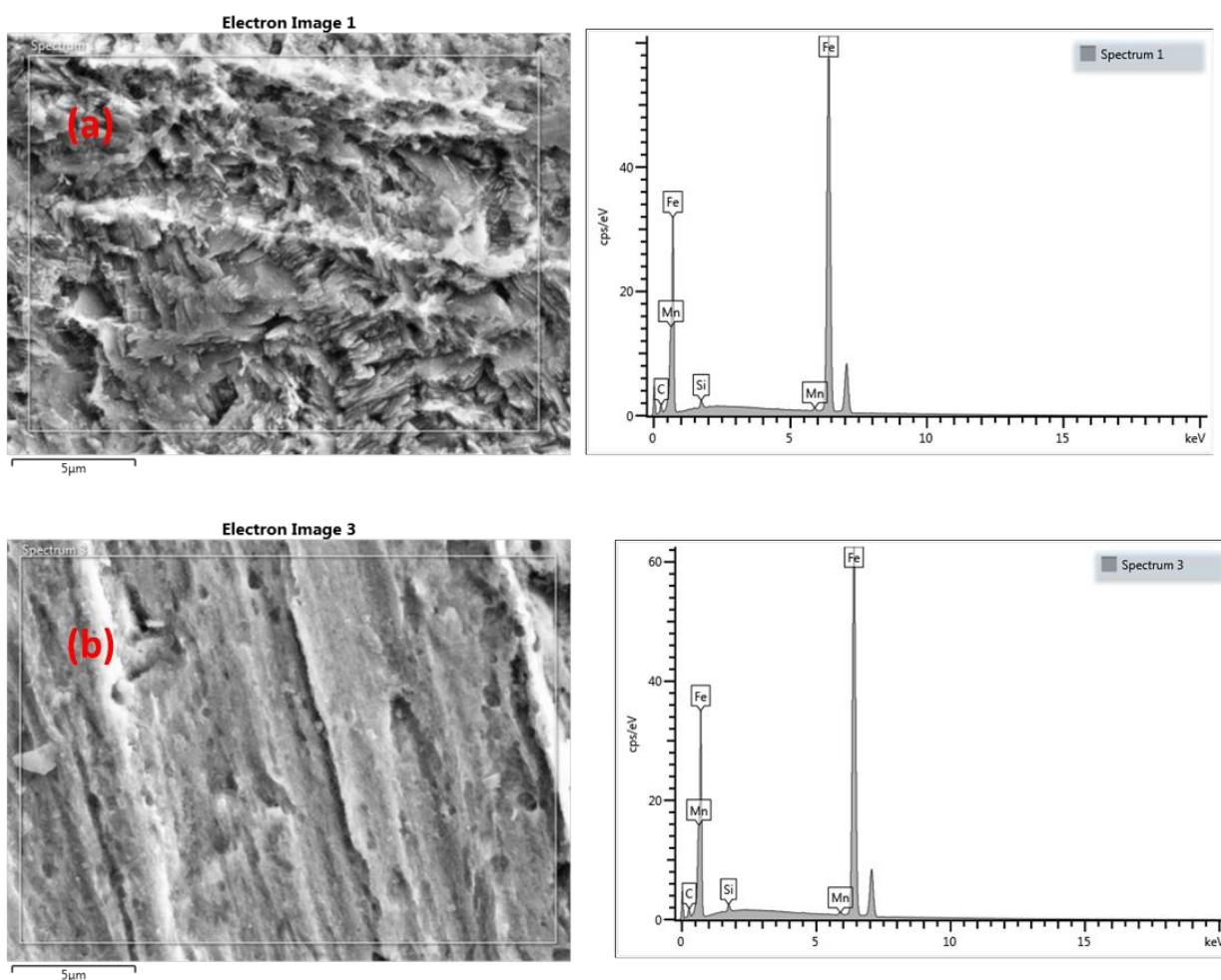


Figure 13 SEM images of mild steel in 1 M HCl (a) uninhibited, scale bar = 5 μm, (b) inhibited 1.0 % w/v EEPN, scale bar = 5 μm

### 3.11 FTIR analysis

The FTIR analysis of the samples was done to identify the functional groups in the material. The adsorption product of the powdered mild steel was carried out to establish that the extract mitigates corrosion from taking place on the mild steel. The IR spectra of the EEPN and the adsorption product of the powdered mild steel are shown in Figure 14 and 15. From the result obtained, it shows that corrosion inhibition occurs through the adsorption process. Table 5 shows the bonds present in EEPN and adsorption product of the powdered mild steel. The EEPN shifted from  $3421$  to  $3396\text{ cm}^{-1}$ . The shifting in the frequencies may reveal that the active phytochemical constituents in EEPN molecules bind to the surface of the metal. This led to form a protective metal-inhibitor complex to reduce more metal disintegration in the acidic media. The adsorption between extract and mild steel which occurs through the functional groups was as a result of the changes in the adsorption bands. The FTIR of the EEPN revealed oxygen and nitrogen atoms functional groups which is one of the factors responsible for the mitigation of corrosion [9].

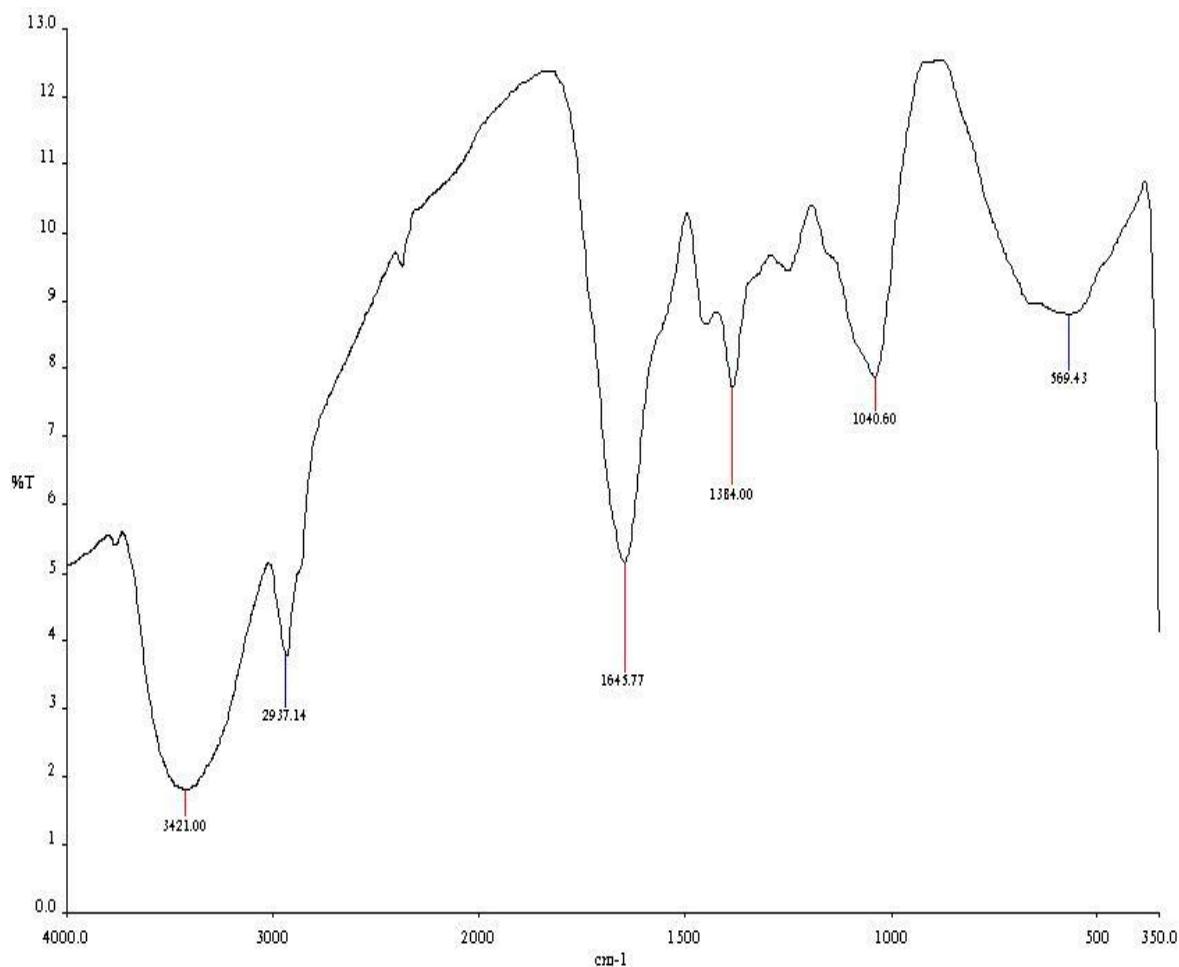


Figure 14 IR spectrum of EEPN

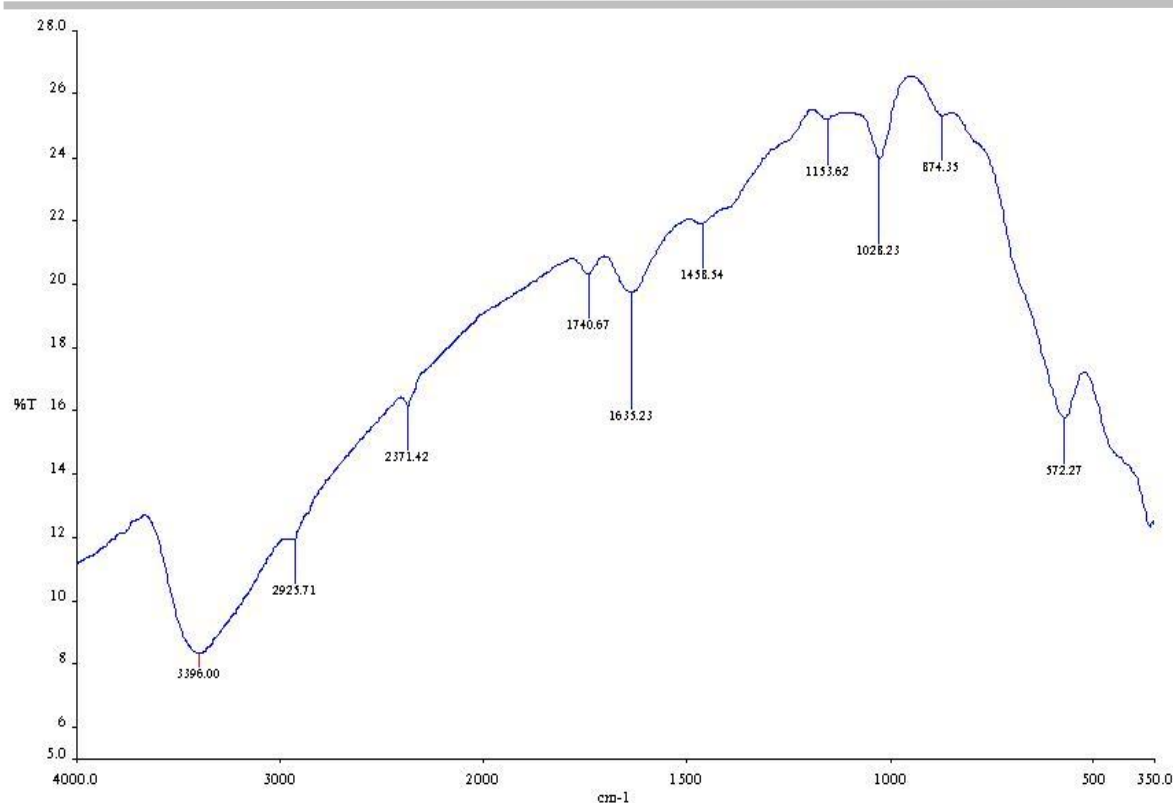


Figure 15 IR spectra of dried solid adsorption product of EEPN and mild steel powder

Table 5 Frequencies of adsorption of FTIR by EEPN

EEPN		Dried solid adsorption product of EEPN	
Wavenumber/cm <sup>-1</sup>	Assignment	Wavenumber/cm <sup>-1</sup>	Assignment
3421	O-H stretch	3396	O-H stretch
2931.42	C-H stretch	2925.71	C-H stretch
1645.77	C=C stretch	2571.42	C-H stretch
1384	C=N stretch	1633.23	C=C stretch
1040.60	O-H stretch	1458.54	Methyl C-H
		1155.62	C-O stretch

#### 4. Conclusion

The EEPN acts as a good inhibitor for the corrosion of mild steel in acidic medium. The I.E of the EEPN increases with an increase in temperature as the concentration of the inhibitor increased. The corrosion inhibition occurs as a result of the uptake of the extract's phytochemical constituents on the mild steel surface thus, blocking the active sites via chemical adsorption. The extract obeyed Langmuir, Freundlich, and Temkin adsorption isotherm from the experimental data fit. The value of  $E_a$  gotten in the inhibited was lesser than that of the uninhibited, which fosters supports the chemical adsorption suggested. The free energy value gotten for the adsorption was negative, revealing the spontaneity of the adsorption process. The enthalpy positive value of adsorption implies that the process is endothermic, and the sorption of the extract on the mild steel surface occurs. The entropies negative values suggest

that the system exhibits random behavior. The negative  $\Delta S^\circ$  values were negative suggesting that the adsorption was enthalpy-driven due to the exothermic enthalpy of adsorption for the EEPN. The result shows that as the molarity of potassium iodide increases, the corrosion rate decrease, and the inhibition efficiency increases. The surface morphology of the accumulated protective film on the surface of the mild steel established the high performance of the extract's inhibitive effect. The uninhibited product on the surface of the mild steel in *Parquetina nigrescens* extract was characterized by SEM and FTIR.

#### Declarations

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##### Declaration of interest

None

##### Availability of data and materials

Data are contained within the article

##### Code availability

Not applicable

##### Authors' contribution

**Olayinka O. Oluwasina and Emmanuel F. Olasehinde:** Conceptualization, **Olayinka O. Oluwasina:** writing-original draft preparation, **Olayinka O. Oluwasina and Emmanuel F. Olasehinde:** methodology, **Olayinka O. Oluwasina and Emmanuel F. Olasehinde:** writing-review and editing, **Emmanuel F. Olasehinde:** supervision, **Olayinka O. Oluwasina, Emmanuel F. Olasehinde and Tolulope E. Adedayo:** data curation.

#### References

- [1] Geethamani P, Kasthuri PK (2016) The inhibitory action of expired asthalin drug on the corrosion of mild steel in acidic media: A comparative study. J. Taiwan Inst. Chem. Eng 63:490-499.
- [2] Singh AK, Chugh B, Saha SK, Banerjee P, Ebenso EE, Thakur S, Pani B (2019) Evaluation of anti-corrosion performance of an expired semi synthetic antibiotic cefdinir for mild steel in 1 M HCl medium: An experimental and theoretical study, Results Phys 14, 102383.
- [3] Loto CA, Mohammed AI (2000) The effect of anacardium occidentale (cashew) juice extract on the corrosion of mild steel in hydrochloric acid, J. Corr. Prev. Control 2:50-63.
- [4] Karthik R, Muthukrishnan P, Shen-Ming C, Jeyaprabha B, Prakash P (2015) Anti-Corrosion Inhibition of Mild Steel in 1M Hydrochloric Acid solution by using Tiliacora acuminate leaves Extract, Int. J. Electrochem. Sci 10:3707-3725.
- [5] Ameen MA, Fekry AM (2011) Corrosion inhibition of mild steel by natural product compound. Prog Org. Coat 71:343-349.
- [6] Akinbulumo OA, Odejobi OJ, Odekanle EL (2020) Thermodynamics and Adsorption Study of the Corrosion Inhibition of Mild Steel by *Euphorbia heterophylla* L. Extract in 1.5 M HCl, Results Mater 5 100074.
- [7] Kavitha N, Manjula P, Anandha N (2014) Synergetic effect of C. papaya leaves extract-Zn<sup>2+</sup> in corrosion inhibition of mild steel in aqueous medium, Res. J. Chem. Sci 8:88-93.
- [8] Njoku CN, Onyelucheyi OE (2015) Response surface optimization of the inhibition efficiency of *Gongronema latifolium* as an inhibitor for aluminium corrosion in HCl Solutions, Int. J. Mat. Chem 1:4-13.
- [9] Tan B, Xiang B, Zhang S, Qiang Y, Xu L, Chen S, He J (2021) Papaya leaves extract as a novel eco-friendly corrosion inhibitor for Cu in H<sub>2</sub>SO<sub>4</sub> medium. J. Colloid Inter Sci 582:918-931.
- [10] Abro IA, Abro MI, EH Assad M, Rahimi-Gorji M, Hoang NM (2020) Investigation and evaluation of neem leaves extract as a green inhibitor for corrosion behavior of mild steel: An experimental study. J Mech Eng Sci 2020 0(0) 1-10.
- [11] Alaneme KK, Olusegun SJ, Adelowo OT (2015) Corrosion inhibition and adsorption mechanism studies of *Hunteria umbellata* seed husk extract on mild steel immersed in acidic solutions, Alexandria Eng. J 10:45-51.
- [12] Manimegalai S, Manjula P (2015) Thermodynamic and adsorption studies for corrosion inhibition of mild steel in aqueous media by *Sargassum swartzii* (Brown algae), J. Mat. Environ. Sci 6:1629-1637.
- [13] Omowumi TK, Musa TY (2017) *Parquetina nigrescens* leaves: chemical profile and influence on the physical and biochemical indices of sexual activity of male Wistar rats. Journal of Integr. Med 15:64-76.
- [14] Moses SO, Oladipupo AL, Rebecca MH, William NS (2014) The volatile constituents of *Parquetina nigrescens* from Southwestern Nigeria, Nat. Prod. Commun 9:857-858.

- [15] Oloyede GK, Ali MS, Lateef M, Oladunmoye RA, Famoyegun JD (2018) Enzyme and oxidation inhibitory activities of cardenolides from leaves of *Parquetinanigrescens*. Academia Arena 10:24-33.
- [16] Onyeka EU, Nwabekwe IO (2007) Phytochemical profile of some green leafy vegetables in S.E. Nigeria. Niger Food J 25:67–76.
- [17] Olasehinde EF, Olusegun SJ, Adesina AS, Omogbehin SA, Momoh-Yahayah H (2013) Inhibitory action of Nicotiana tabacum extracts on corrosion of Mild Steel in HCl: Adsorption and Thermodynamics Study". Nat. Sci 11:83-90.
- [18] Ahamed I, Quraishi MA (2010) Mebendazole: new and efficient corrosion inhibitor for mild steel in acid medium. Corros Sci 52:651–6.
- [19] Foud AS, Al-Sarawy AA, Ahmed FS, Zhang ST, Pei CI, Hou B (2008) Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium. J Appl Electrochem 38:289–95.
- [20] Karthik R, Muthukrishnan P, Shen-Ming C, Jeyaprabha B, Prakash P (2015) Anti-Corrosion Inhibition of Mild Steel in 1M Hydrochloric Acid solution by using Tiliacora acuminate leaves Extract. Int. J. Electrochem. Sci 10:3707–3725.
- [21] Reda SA, Ismail HI, Mohamed AA (2020) Expired Indomethacin Therapeutics as Corrosion Inhibitors for Carbon Steel in 1.0 M Hydrochloric Acid Media. J. Bio- Tribo-Corros 6, 114.
- [22] Fouda AS, Tawfik H, Badr AH (2012) Corrosion inhibition of mild steel by Camellia Sinensis extract as green inhibitor. Adv. Mater. Corros 1:1-7.
- [23] James AO, Oforka NC, Abiola OK (2006) Inhibition of Aluminium (3SR) corrosion in hydrochloric acid by pyridoxol hydrochloride. Bull. Electrochem 22:111-116.
- [24] Ekpe UJ, Okafor PC, Ebenso EE (2004) Inhibition of the acid corrosion of aluminium by some derivatives of Thiosemicarbazone, Bull. Chem. Soc. Ethiopia 18:181-192.