

Action of Matured Seeds' Extracts Of *Persea Americana* var. *Americana* in Dil. HCl. for Corrosion Inhibition on Mild Steel

Anthony C. Ehiemere, Chiza A. Ogbuji, Conrad Enenebaku

CORRESPONDING AUTHOR: Anthony C. Ehiemere
Department of Chemistry, Abia State Polytechnic, Aba, Nigeria
Email: chimex4tops@yahoo.com

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ABSTRACT

An investigation was carried out on the ability of aqueous extracts from matured *Persea Americana* var. *Americana* seeds for their corrosion inhibition potentials on mild steel in 1 M HCl conditions using gravimetric methods, as well as potentiodynamic tests and impedance measurements. The tests were considered at room temperature for 24 hours, and also for higher temperatures from 40°C to 70°C for 1 hour. The results showed that seeds' extracts have appreciable corrosion inhibition potentials which decreased with increase in temperature. Inhibition efficiency showed that it increased with increase in inhibitor concentration across the same temperature, and similarly decreased with increase in temperature within the same concentration range. The maximum inhibition value was 86.49% in 24 hours, and 44.36% for 40°C and 75.46% for 70°C. The experimental data were in consonance with the Langmuir isotherm suggesting that the extract constituents were adsorbed on the steel surface. The Arrhenius equations showed that they increased generally showing that physisorption rather than chemisorptions is prevalent. The values of the heat of adsorption are all negative for temperatures at 40°C, indicative of the fact that inhibition efficiency decreases with rise in temperature, a proof that the inhibition trend was physisorption. At temperatures of 70°C, the values are mixed, some negative and some positive. This indicates that both physisorption and chemisorptions are effective. The result from potentiodynamic tests shows that reduction in current potential in the presence of the inhibitor at both concentrations show it is a mixed inhibitor.

Keywords: Arrhenius equation, Corrosion, Corrosion inhibition, Langmuir isotherm, *Persea Americana*.

INTRODUCTION

Corrosion of a metal is said to be due to chemical or electrochemical reactions when it comes in contact with matters present in its environment.

[1]. Corrosion is one of the worst enemies of an industry like a cancer cell it often slowly develops for many years and remains undetected. Its effects are felt in many areas of life where its economic importance is massive, example in supply of water. [2]. Corrosion in steel or cast iron water distribution pipes, is not only responsible for the destruction of pipe material but also for deterioration of potable water quality due to unwanted chemical and biochemical reactions occurring in the distribution systems.

[3]. However, corrosion can be controlled by suitably modifying the environment which stifles the anodic or cathodic reaction or both, and this is achieved by the use of inhibitors.

[4]. Atmospheric corrosion is a major problem for the application of engineering metals in many types of service. As a result there is an ongoing effort to understand this phenomenon and develop standards that can be used to lighten the severity of corrosion processes in service conditions.

[5]. Mild steel (low carbon steel) has composition of 0.05%–0.25% carbon and up to 0.4% manganese. [6]. The building industry frequently uses mild steel in construction because of its ductility and malleability. It is the least expensive of all steel and the most common steel used. Used in nearly every type of product created from steel, it is weldable, very hard and, although it easily rusts, very durable.

Corrosion inhibitors are substances which, when added to a corrosion system decreases or eliminates anodic dissolution. In recent years, most researchers are focusing on natural products as corrosion inhibitors. This is because, organic and inorganic inhibitors are known to be toxic, expensive, and not readily available. *Persea Americana* is available in great abundance in Aba and its environs as they can be found in almost every native compound, and also, in many private compounds in the city. *Persea Americana* (Avocado pear in English; Ube Bekee in vernacular) seeds are rather big. Many a time, this plant parts constitute parts – and – parcels of garbage which litter the town and country sides. This is because, the fruits are so much in abundance that the supply is always much more than the demand and since their seeds are not edible, they somehow, are seen and regarded as nuisances.

[7]. There are generally considered to be three putative botanical varieties within *P. Americana*: var. *Americana*, var. *drymifolia*, and var. *nubigena*. Differences between them relate primarily to ecological preferences and fruit characteristics, though even within the same botanical variety the size, shape, rind, flesh and seed of the fruit is highly variable. Variability in seed size is very common even within the same plant. This specie chosen for this work is var. *Americana*, the most common one around Aba and its environs.

Inhibitors cover a wide field of anti-corrosion measures. A lot of work on the subject is concerned with preventing the attack of specific chemicals on certain metals during manufacturing, transport or storage. Most proposed inhibitors are natural plant or animal products, dyes, industrial by-products or pure chemical compounds.

EXPERIMENTAL

Preparation of Specimens

The mild steel sample was cut into various pieces of the same measured dimensions of 1mm x 50mm x 40mm.

Holes were drilled in the coupons to enable the insertion of a hanger. The coupons were further wet polished with silicon carbide abrasive paper (from grade 800 – 1600), degreased in absolute ethanol, rinsed in acetone, weighed and stored in moisture-free desiccator prior to corrosion studies.

Method of extraction

Stock solutions of the plants extracts were prepared by reflux boiling of 20 g of the dried, ground, filtered, and weighed sample of *Persea Americana* var. *Americana* for 3 hours in a round-bottomed flask, allowed to cool at room temperature, and filtered using weighed white handkerchief, and stored. From the respective stock solutions, inhibitor test solutions were prepared with concentrations of 100, 500, and 1100 mg L⁻¹ in the corrodent. The electronic weighing instrument used is OHAUS brand.

Weight Loss Determination

Gravimetric methods were conducted on mild steel coupons of stated dimensions. In the weight loss experiment, four reaction vessels (for each plants specie) labeled BL for blank, and A₁ – A₃ for samples containing various masses of the inhibitor in 1.0 M of the corrodent. The mild steel coupons were carefully weighed and properly tagged to avoid mix up. These coupons were suspended (under total immersion conditions) in the reaction vessels containing 200 ml of the test solutions with the aid of twine and broom sticks. All tests were made in aerated solutions. In the first experiments for each corrodent, the coupons were retrieved after 24 hours.

The other experiments were for the effects of temperature in which the enabling ranges were for 40, and 70 °C, respectively, for 1 hour.

In each case, the retrieved coupons were scrubbed with bristle (smokers) brush under water, dipped in absolute ethanol, rinsed with water, dried in acetone, and reweighed. The weight loss was a simple difference between the initial mass and the final mass retrieved from the corrodent solutions.

The evaluated results were for (i) Inhibition efficiency, η (I.E.) in percentage, given by

$$\eta\% = \left(1 - \frac{\Delta M_{SP}}{\Delta M_{IN}}\right) \times 100 \quad (1)$$

where ΔM = mass loss; SP = sample; IN = inhibitor; and (ii) Corrosion rate, ρ , given by

$$\rho = \frac{KW}{DAT} \quad (2)$$

where K = rate constant (534 mpy; mils per year, 1 mil = 10⁻³ in); W = mass loss in mg; D = density of the mild steel coupon (7.85 g cm⁻³); T = immersion time(h); A = exposed area of the coupon (0.1911cm²).

Electrochemical measurements

Electrochemical tests were conducted in a conventional three-electrode corrosion cell, using a V3 Potentiostat/Galvanostat, coupled to a PC, running on the Powersuite and Powersine software. A graphite rod and saturated calomel electrode (SCE) served as counter and reference electrodes respectively. Test metal specimens were fixed in epoxy resin with a surface area of 1 cm² exposed to the test solution. Measurements were in aerated and unstirred solutions at the end of 1800s of immersion at 30±1 °C. Each test was run in triplicate and the mean values of the measured parameters presented.

Impedance measurements were carried out using signal amplitude perturbation of 5 mV at the corrosion potentials (E_{corr}) and frequency range 100 kHz - 0.1 Hz. The resulting impedance data were analyzed using Zsimpwin 3.0 software. Potentiodynamic polarization measurements were performed at a scan rate of 0.333 mV/s and potential range ±250 mV versus corrosion potential.

RESULTS AND DISCUSSION

The graphs shown in Figs. 1 and 2 below show the results gotten when corrosion rate and inhibition efficiency is each plotted against concentration values of 100, 500, and 1100 mg L⁻¹. The results show that matured *P. Americana* seed extracts effectively inhibits corrosion on mild steel coupon in 1.0 M HCl solution. In the case of corrosion rate, the result shows that there is a marked difference between the solutions without inhibitor from that with inhibitor. For inhibition efficiency, it shows that increase in inhibitor concentration leads to a corresponding increase in inhibition efficiency.

Figs. 3 to 6 show plots of corrosion rate and inhibition efficiency respectively against concentration at elevated temperatures. Fig. 3 is corrosion rate plotted against time at 313 K. The plot shows that just as in Fig. 1, for

the solution without inhibitor, the rate of corrosion is fastest. However, the other specimens with inhibitors had improved corrosion rate, probably due to increase in temperature. It is known that increase in temperature has a corresponding increase in corrosion rate as increase in temperature increases the rate of a chemical reaction. The same observation is made for the experiment at 343 K (Fig. 5).

The values for inhibition efficiency follow a corresponding trend. Increase in inhibitor efficiency leads to a corresponding increase in inhibition efficiency, though the values are less than the case of the experiment at room temperature (Fig. 2). The same is observed for Fig. 6.

The results clearly showed that *P. Americana* seed extracts can inhibit the corrosion of mild steel in 1.0 M HCl. Quantitative evaluation of the inhibitive effect of matured *P. Americana* seeds on mild steel corrosion was achieved by comparing the corrosion rates in the absence and presence of the inhibitor. There is generally, an increase in inhibition efficiency for all the considered cases.

[8]. From these results, it can deduced that the corrosion rate increases in the blank solution with rise of temperature, but in the presence of the inhibitors, the dissolution of mild steel is widely retarded. The inhibitive efficiency of the inhibitor however, changes with the rise of temperature. Despite the variance, it can be concluded that the plant is a good inhibitor at even high temperatures since the corresponding rates from blank to presence of inhibitor vary widely.

Temperature Considerations

There is an observed general increase in corrosion rates as temperature increases and a decrease in corrosion rates as inhibitor concentration increases. This could be ascribed to the fact that increase in temperature has a corresponding effect in rates of corrosion for media where hydrogen gas evolution accompanies corrosion resulting in higher dissolution rates, while increase in inhibitor concentration tends to resist this trend. Higher rates of hydrogen gas generation increasingly agitate the metal/corroder interface and could hinder inhibitor adsorption or perturb already adsorbed inhibitor, especially when the interaction between the metal and the inhibitor is relatively weak.

[9]. This is a trend observed in most organic corrosion inhibitors wherein the trend is attributed to physical

rather than chemical adsorption of the inhibitor on the corroding metal surface.

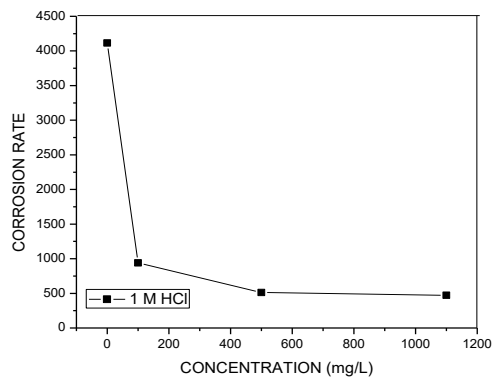


Figure 1: Corrosion Rate v Concentration for coupons at room temperature for 24 h

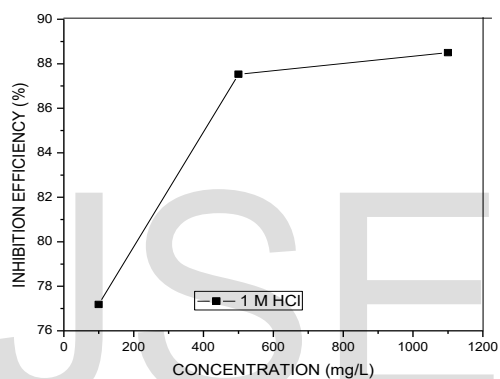


Figure 2: Inhibition Efficiency v Concentration for coupons at room temperature for 24 h

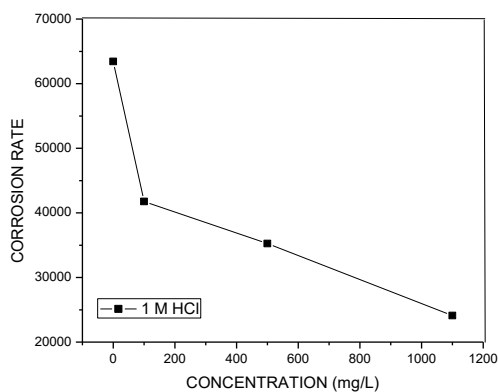


Figure 3: Corrosion Rate v Concentration for Coupons at 313k for 1h

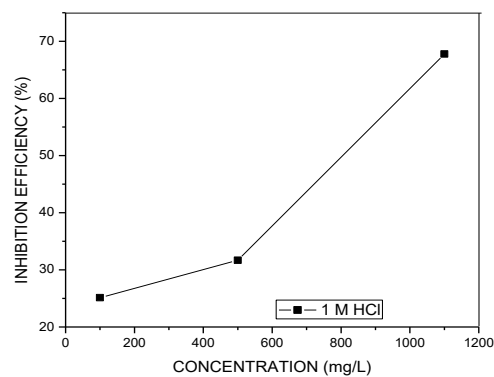


Figure 4: Inhibition Efficiency v Concentration for coupons at 313 K for 1h

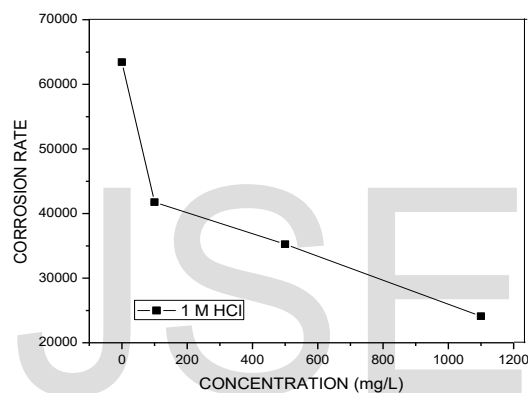


Figure 5: Corrosion Rate v Concentration for Coupons at 343K for 1 h

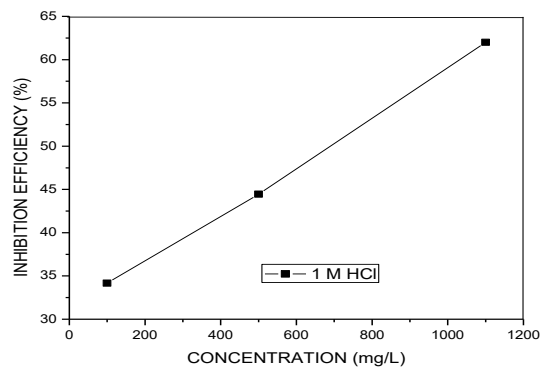


Figure 6: Inhibition Efficiency v Concentration for Coupons at 343 k for 1 h

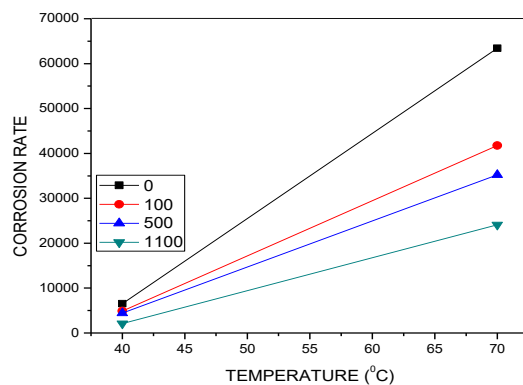


Figure 7: Variation of Corrosion Rate with Temperature at different concentration

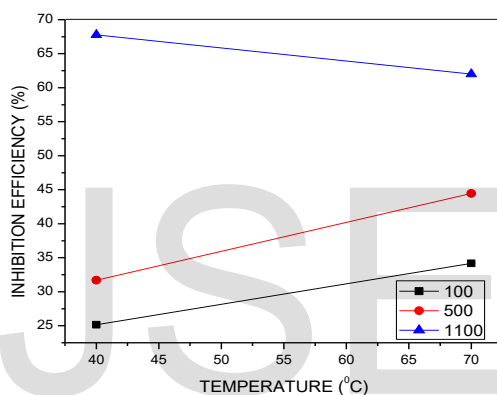


Figure 8: Variation of Inhibition Efficiency with temperature at different concentrations

The Langmuir Isotherm and the Arrhenius equation

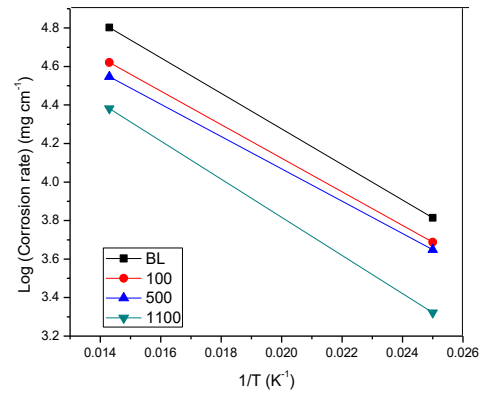


Figure 9: Arrhenius plot for mild steel in 1.0 M HCl environment and at different temperatures

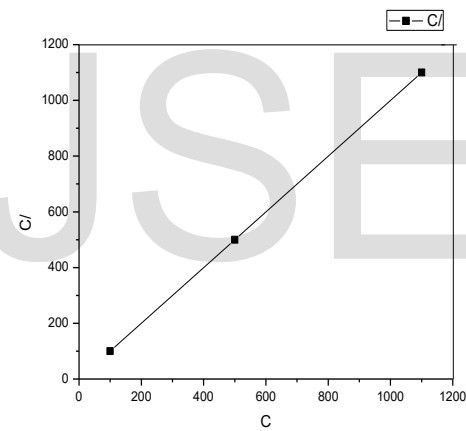


Figure 10: The Langmuir plot

The **Langmuir adsorption** isotherm was found to be the best description of the adsorption behavior of the studied inhibitor. The data fit straight line, with slope nearly equal unity, indicating that this compound adsorbs according to Langmuir adsorption isotherm. ΔG_{ads} is not accessible because of the unknown molecule responsible for the inhibition process. [10]. In such case, the inhibition is explained as a synergistic intermolecular effect of the various components of the natural substances present.

The **Arrhenius equation** ($k = A \exp (-E_a/RT)$) can be related to corrosion rate (q) and temperature (T), where E_a is the activation energy, A the Arrhenius pre-exponential factor, and R the universal gas constant.

$$E_a = (ln A - ln k) RT \quad (3)$$

The apparent activation energies for mild steel corrosion from Arrhenius equation is as follows:

$$\log \frac{q_2}{q_1} = \frac{E_a}{2.303RT} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

where q = corrosion rate; and T = temperature.

From the plots in Fig. 9, it can be seen that activation energy increased generally.

[11]. This gives further credence to the fact that physisorption rather than chemisorption is the underlying factor operating in this inhibitor specie. The increase in activation energy from the blank reaction to the inhibited reaction is also a pointer that physical rather than the chemical adsorption tendencies are favored.

Potentiodynamic polarization measurement (PDP)

Potentiodynamic polarization curves for mild steel in 1 M HCl containing different concentrations of PA at 30 °C are depicted in Fig. 11. All the corresponding electrochemical parameters like the corrosion current densities (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slopes (b_c) and anodic Tafel slopes (b_a) obtained from polarization curves are shown in Table 1. The mild steel specimen is seen to exhibit rapid dissolution with no sign of transition to passivation within the studied potential range. The behavior of the polarization curves in 1 M HCl environment (Fig. 11) shows that the presence of PA inhibitor shifts the cathodic and anodic curves towards the area of lower current densities. Again, addition of PA into the acidic solution has no pronounced effect on the corrosion potential (E_{corr}) in each case. Results presented in Table 1 reveal that the highest displacement in E_{corr} value in the studied acidic

solutions was less than 85 mV, for this reason, PA is regarded as a mixed-type inhibitor.

The data in Table 1 show that the corrosion current density decreased significantly in the presence of PA inhibitor compared to the uninhibited solution and also decreased with an increase in the concentration of the extract. The inhibition efficiency was calculated using the equation:

$$IE\% = \left(\frac{I_{corr(bl)} - I_{corr(inh)}}{I_{corr(bl)}} \right) \times 100 \quad (5)$$

where $I_{corr(bl)}$ and $I_{corr(inh)}$ represents the corrosion current density in the absence and presence of the inhibitor, respectively (Adsorption and corrosion inhibiting effect of riboflavin on Q235 mild steel corrosion in acidic environments). In this environment the highest inhibition efficiency obtained is 92.1% at a concentration of 1000 mg/L at 30 ±1°C.

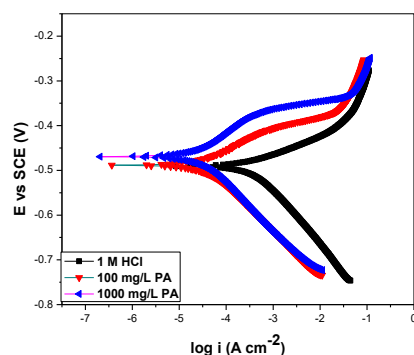


Figure 11: Potentiodynamic polarization curves of mild steel in 1M HCl in the absence and presence of matured *Persea Americana* seed extract.

TABLE 1: Polarization Parameters for Mild Steel in HCl and H₂SO₄ in the absence and presence of matured *Persea Americana* seed extract.

SYSTEM	E _{corr}	I _{corr}	Θ	I.E. %
BLANK	-503.4	183		
100 mg L ⁻¹	-504.9	56.2	0.693	69.3
1000 mg L ⁻¹	-456.9	14.8	0.921	92.1

Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy measurements was carried out in order to reveal the kinetics of the electrochemical processes taking place at the metal/solution interface, and how they were modified by PA inhibitor. Fig. 12 represents the Nyquist plots of the impedance response of mild steel in 1 M HCl environment in the absence and presence of various concentrations of PA inhibitor. As can be seen, the obtained plots comprise of only one depressed capacitive semicircle in the high-frequency region, which is attributed to one time constant in the Bode plots. The observed depression of the Nyquist semicircle with center under the real axis is typical for solid metal electrodes that show frequency dispersion of the impedance data.

[12]. This is due to roughness and inhomogeneity of the metal surfaces. The transfer function can be represented by a solution resistance R_s , shorted by a capacitor C that is placed in parallel to the charge transfer resistance R_{ct} :

$$Z_{(\omega)} = R_s + \left(\frac{1}{R_{ct}} + j\omega C \right)^{-1} \quad (6)$$

This transfer function is applicable, however, only for homogeneous systems with one time constant when the center of the semicircle lies on the abscissa and cannot account for the depression of the capacitive semicircle. When a non-ideal frequency response is present, the capacitor is replaced by a **constant phase element** (CPE). The application of such a CPE accounts for the deviations from ideal dielectric behavior and is related to surface inhomogeneities. The impedance, Z , of the CPE is:

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \quad (7)$$

where Q and n depicts the CPE constant and exponent, respectively, $j^2 = -1$ is an imaginary number, and ω is the angular frequency in rad s^{-1} ($\omega = 2\pi f$ when f is the frequency in Hz), CPE can represent resistance ($Z_{CPE} = R$, $n = 0$), capacitance ($Z_{CPE} = C$, $n = 1$).

[13]. To determine the values of the corresponding impedance parameters shown in Table 3, the obtained impedance spectra were determined using an equivalent circuit model (Fig. 13) which has been employed previously to model the metal/acid interface. The diameter of the Nyquist semicircle is related to charge transfer resistance (R_{ct}). The introduction of PA

inhibitor into 1 M HCl solution as shown in Fig. 12 resulted to an increase in the diameter of the Nyquist semicircle in each case which indicates inhibition of the corrosion process. Increase in the concentration of PA inhibitor improved the magnitude of the impedance response, but did not affect the mechanism of the process. Furthermore, the C_{dl} decreased in the presence of the inhibitor. Such decrease normally results from a reduction in the local dielectric constant and/or an increase in the double layer thickness. The behavior may be attributed to the adsorption of the inhibitor species on the metal/solution interface. The observed phenomenon is in line with the Helmholtz model, given by the equation

$$C_{dl} = \frac{\epsilon \epsilon_0 A}{\delta} \quad (8)$$

where ϵ_0 is the vacuum permittivity and ϵ the relative permittivity of the film. Accordingly, the trend of C_{dl} means that the observed increase in R_{ct} resulted from the formation of an adsorbed layer of PA inhibitor on the metal/solution interface, which protects the metal surface from corrosion.

The inhibition efficiencies ($IE\%$) for different inhibitor concentrations were calculated from Nyquist plots using the equation:

$$IE\% = \left(\frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \right) \times 100 \quad (9)$$

Where R_{ct} and $R_{ct(inh)}$ denotes charge transfer resistance in the absence and presence of the inhibitor.

Table 2 Electrochemical Impedance Parameters of Mild Steel in HCl in the Absence and Presence of matured *Persea Americana* (PA) seed extracts.

System	R _s (Ω cm ²)	R _{ct} (Ω cm ²)	N	C _{dl} (F cm ⁻²)	I.E. (%)
1M HCl	1.659	102.7	0.89	6.908 E-5	
100 mg/L PA	2.007	270	0.84	7.094 E-5	61.9
1000 mg/L PA	2.923	1100	0.83	7.075 E-5	90.7

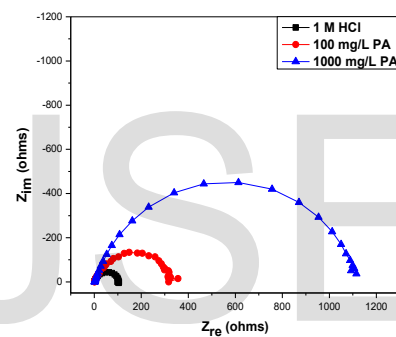


Figure 12: Electrochemical Impedance Parameters of Mild Steel in HCl and H₂SO₄ in the Absence and Presence of matured seed extracts of PA.

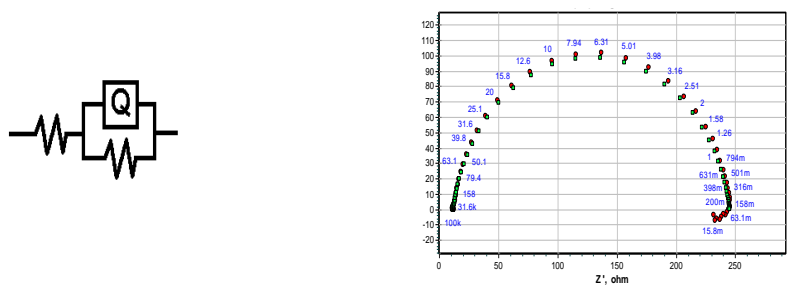


Figure 13: Equivalent circuit model for mild steel with the accompanying experiment fit

TABLE 3: Apparent activation energies and heat of adsorption, for the corrosion of mild steel in 1.0 m HCl solution containing matured *Persea Americana* seed extract in different concentration in the temperatures of 313 and 323 k

	314 K	314 K	343 K	343 K
Conc.(mg/L)	Ea(kJ/mol)	Q _{ads} (kJ/mol)	Ea((kJ//mol)	Q _{ads} ((kJ//mol)
Blank	65.52		482.48	
100.00	249.35	-0.2881	455.20	0.08396
500.00	326.91	-0.3389	438.67	0.06802
1100.00	225.58	-0.1619	517.22	-0.03154

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CONCLUSION

From the discussions of the experimental data of this work, it could be concluded that matured *Persea Americana* seed extracts acts as an inhibitor for mild steel corrosion in 1M HCl solution. The inhibition efficiency increases with increase in concentration of matured *Persea Americana* seed extract, but slightly decreases with an increase in temperature at higher concentration of 1100mg/l of the inhibitor. The corrosion inhibition of the matured *Persea Americana* seed extract showed both physical and chemical interaction between the components of the inhibitor and the mild steel surface. This was evident from the values of Q_{ads} which was negative which is suggestive of strong adsorption of the inhibitor components on the mild steel surface and at some point positive which is suggestive of chemisorptions. The potentiodynamic polarization (PDP) results revealed that matured *Persea Americana* seed extract is a mixed inhibitor.

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1. Anthony C. Ehiemere, Department of Chemistry, Abia State Polytechnic, Aba Nigeria
2. , Chiza A. Ogbuji, Department of Food Science and Technology, Abia State Polytechnic. Aba. Nigeria
3. Conrad Enenebaku, Department of Chemistry, Federal University of Technology, Owerri, Nigeria

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