

## Corrosion Inhibition of Mild Steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> Using Ethanol Extract of *Funtumia elastica*

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**ABSTRACT.** The adsorption and corrosion inhibitive effect of the ethanol extract of *Funtumia elastica* (FE) leaves on mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> was studied using gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopic techniques. As well as Fourier transform infrared spectroscopy and computational methods. The gravimetric and electrochemical studies revealed that FE is an adsorption inhibitor. The potentiodynamic polarization result showed that the inhibitor is a mixed type corrosion inhibitor for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>, inhibiting both the cathodic and anodic partial reactions. Density functional theory calculations were performed to model the electronic structures of some selected extract constituents (conessine, and ascorbic acid) to confirm their inhibiting potential and established their individual contributions to the observed inhibiting effects.

## INTRODUCTION

Corrosion is the gradual degradation and destruction of materials especially metals when exposed to the environment. Corrosion occurs because most metals tend to return to their thermodynamically more stable compounds with time. Corrosion control of metals is of economic and environmental importance. The use of natural materials as corrosion inhibitors is one of the best options for protecting metals from corrosion attack. These materials have the advantage of being non-toxic, cheap, easily obtainable and environmentally friendly [1-10]. It has been reported that these natural materials contain abundant phytochemicals (tannins, alkaloids, amino acids, flavonoids, phenols saponins etc.) whose field of application can be extended from medicinal importance to material protection as an alternative to the more hazardous chemicals used as corrosion inhibitors [11-18]. Most of these materials are known to contain a centre for  $\pi$ - electrons and such functional groups as -OR-, -C=C-, -OH, -NH<sub>2</sub>, -NR<sub>2</sub>, -SR, and -COOH which provide electrons that facilitate the adsorption of the material on the metal surface. It has also been proven that the presence of hetero atoms such as oxygen sulphur and nitrogen enhances the adsorption process [19-23].

A number of researches have been carried out on the use of natural products as corrosion inhibitors for metals. Extracts of *Piper guineense* [24, 25], *Telferia occidentalis*, *Azadirachta indica*, *Hibiscus sabdariffa* [26], *Ocimum gratissimum* [27], *Chamaemelum-mixtum*, *Nigella sativa* L [28], *Wrightiatinctoria*, *Ipomoea triloba* [7] and *Lupinus albus* [29] have been investigated for their corrosion inhibition effects on different metals. All the studied extracts proved to be active against the corrosion of the studied metals.

In the present study, the adsorption and corrosion inhibiting effect of ethanol extract of *Funtumia elastica* (FE) on mild steel in sulphuric acid solution has been extensively studied using both experimental and computational methods. Gravimetric and electrochemical methods of monitoring corrosion were employed. The adsorption properties were studied using Fourier Transform Infrared Spectroscopy. Due to the complex nature of the inhibitor material, experimental

determination of the individual phytochemicals contribution to the overall corrosion inhibition was not possible; hence we performed theoretical computation within the framework of density functional theory (DFT). This enabled us to ascertain the individual contributions of the inhibitor constituents to the overall corrosion process. Our approach includes analysis of the molecular electronic structures of the important phytochemical constituents of the extract material searching the mechanism of interaction and computing their respective adsorption energies.

## EXPERIMENTALS

**Materials preparation:** The mild steel specimen used for the experiment has the following weight composition C – 0.05%, Mn – 0.6%, P – 0.36%, Si – 0.3% and balance Fe. The aggressive solution was 0.5 M H<sub>2</sub>SO<sub>4</sub>, the plant material (*Funtumia elastica*) was collected from the botanical garden of the Federal University of Technology Owerri and dried under room temperature. Ten (10) grams of the grinded plant material was refluxed for three hours in 96% ethanol. The resulting solution was cooled and triple filtered. The amount of the plant material that was extracted into the solution was quantified by comparing the weight of the residue with the initial weight of the plant material before extraction. Inhibitor test solutions were prepared in the concentration of (50- 1500 mg/L) by diluting the filtrate with 0.5 M H<sub>2</sub>SO<sub>4</sub>.

**Gravimetric measurements:** The gravimetric experiments were performed on test coupons with dimension 3 cm x 3 cm x 0.14cm. These coupons were polished with silicon carbide abrasive paper (from grade #400 to #800) rinsed in distilled water dried in acetone and warm air and stored in an air tight desiccator prior to use. The cleaned and weighed coupons were suspended in 300ml of the different concentrations of the aggressive solution using hooks and rod. The unstirred solutions were maintained at 30 ± 1°C. To determine weight loss with respect to time, the coupons were retrieved at 24-h intervals progressively for 120-h after which they were left un-retrieved for more 216-h making a total of 336-h. When retrieved, the coupons were immersed in 20% NaOH solution containing 200 g/L of zinc dust, scrubbed with a bristle brush washed, dried and re-weighed. The weight loss was obtained as the difference between the weight at a particular time and the initial weight of the coupon before immersion. All tests were run in triplicates to ensure good reproducibility. Gravimetric experiments were also performed on the mild steel after 3-h as a function of temperature. The temperature range used was (30- 60 °C).

**Electrochemical measurements:** Electrochemical tests were carried out on electrodes of dimension 1 cm x 1 cm. The electrodes were fixed in polytetrafluoroethylene (PTFE) rods by epoxy resin in such a way that only one surface of area 1 cm<sup>2</sup> was left uncovered. The exposed area was cleaned as explained in the gravimetric section above. A three conventional glass cell of capacity 400mL was used in a VERSASTSRT 400 complete DC Voltammetry and corrosion system, with V<sup>3</sup> studio software. The counter electrode was graphite rod with saturated calomel electrode (SCE) as the reference electrode. The reference electrode was connected through a Luggin's capillary. Tests were performed on aerated and unstirred solutions at 303K. Impedance measurements were done at corrosion potentials ( $E_{\text{corr}}$ ) over a frequency range of 100KHz – 10 mHz, with signal amplitude of perturbation of 5 mV. Potentiodynamic polarization experiments were carried out in the potential range of ± 250 mV versus corrosion potential at 0.3333 mV/s scan rate. Each test was done in triplicate to ensure good reproducibility of the results.

**Fourier Transform Infrared Spectroscopy Measurements:** FTIR spectra (KBR pellet) were recorded using a Nicolet-Magna IR 560 FTIR spectrophotometer. The spectra of FE powder before and after extraction were recorded. Also recorded was the spectra of the protective films scraped from the surface of the mild steel after 3-h of immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 1500 mg/L of FE by carefully removing the films, mixing it with KBR, and making the pellets.

### Theoretical considerations:

The theoretical calculations were performed using the DFT electronic structure programs VAMP and DMol<sup>3</sup> as contained in the Accelry's material studio modeling 4.0 software.

## RESULTS AND DISCUSSION

**Gravimetric Data:** Gravimetric measurements were carried out to investigate the inhibitive effect of the ethanol extract of FE on the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The data presented are means of triplicate experiments. Figure 1 illustrates the weight loss of mild steel in 7 different concentrations of FE as a function of exposure time, Figure 2 shows the variation of inhibition efficiency with exposure time for mild steel corrosion in the presence of the 7 concentrations of FE studied and Figure 3 shows the variation of weight loss with concentration of FE for mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

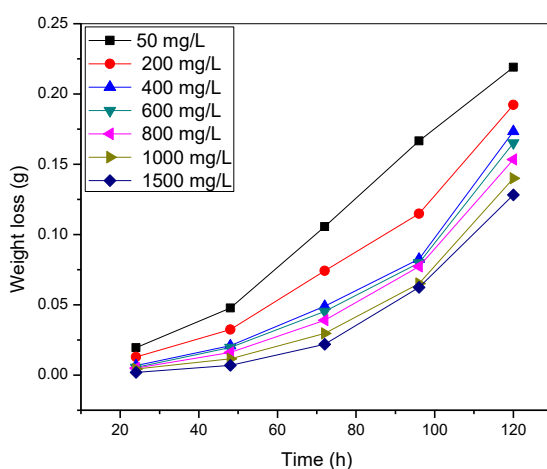


**Figure 1.** Variation of weight loss with time for mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of ethanol extract of FE

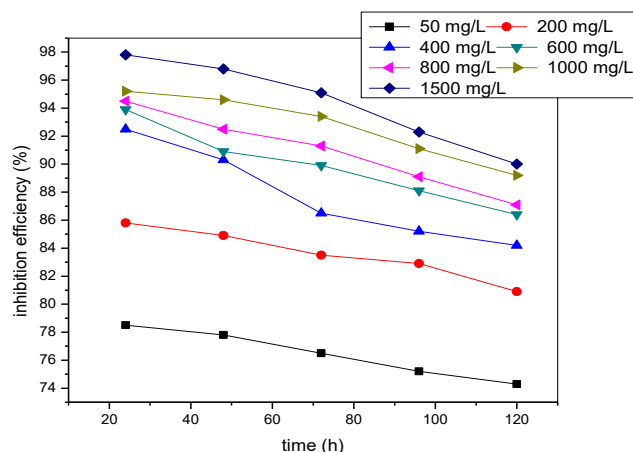


**Figure 2.** Variation of inhibition efficiency with time for mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of ethanol extract of FE.

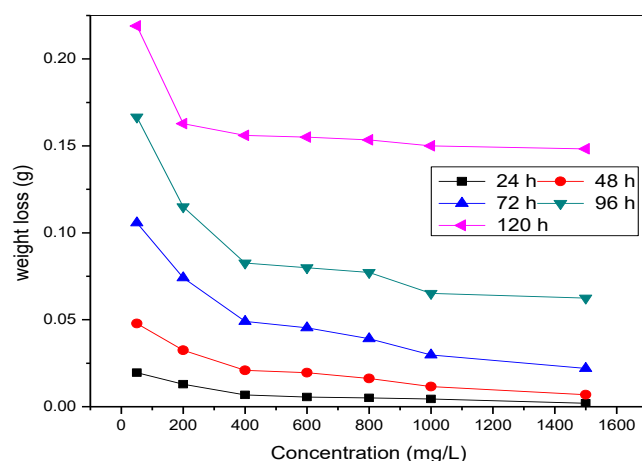


**Figure 3.** Variation of weight loss with concentration for mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of ethanol extract of FE.

The results show that FE extract reduced the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Figure 1 shows that weight loss increased with time for all the concentrations studied, Figure 2 indicates that inhibition efficiency increased with immersion time. The highest inhibition efficiency observed was 97.8% at the concentration of 1500mg/L after 24 h of immersion and the lowest was 52.4% at the concentration of 50 mg/L after 336 h of immersion showing that FE maintained high inhibition efficiency throughout the experiment. Figure 3 shows that corrosion rate decreased steadily with increasing FE concentration.

The inhibition efficiency was quantified by comparing the weight losses of mild steel specimen in the uninhibited ( $\Delta W_{\text{blank}}$ ) and inhibited ( $\Delta W_{\text{inh}}$ ) solution as follows

$$\text{IE\%} = \left( 1 - \frac{\Delta W_{\text{inh}}}{\Delta W_{\text{blank}}} \right) \times 100. \quad (1)$$

where  $\Delta W_{\text{blank}}$  and  $\Delta W_{\text{inh}}$  are the weight losses of mild steel in the absence and presence of inhibitor, respectively.

**Electrochemical Measurements:** Electrochemical impedance spectroscopy and potentiodynamic polarization experiments were undertaken to understudy the inhibitive effects of FE extract on the electrochemical behavior of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Three concentrations of FE extracts (50 mg/L, 600 mg/L and 1500 mg/L) were used for the electrochemical study.

Electrochemical impedance spectroscopy measurements were carried out to give insight into the kinetics of the electrochemical process at the mild steel/acid interface and how this is modified by the addition of FE extracts. Figure 4 gives the Nyquist plot for mild steel corrosion in the absence and in the presence of 50 mg/L, 600 mg/L and 1500 mg/L FE extracts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The Nyquist plots show single semicircles for all systems over the frequency range studied. It can be seen from Figure 4 that the addition of FE extracts increased the size of the semicircle of the Nyquist plot. The high frequency intercept with the real axis in the Nyquist plots is assigned to the solution resistance ( $R_s$ ) and the low frequency intercept with the real axis ascribed to the charge transfer resistance ( $R_{ct}$ ). The impedance data were analyzed by fitting into an equivalent circuit model  $R_s(Q_{dl}R_{ct})$  which has been used previously for data analysis [30,31]. In the equivalent circuit, the solution resistance is shorted by a constant phase element (CPE) that is placed in parallel to the charge transfer resistance. The CPE is used in place of a capacitor to compensate for the deviation from ideal homogeneous nature of the surface of the electrode. The impedance of the CPE is given by

$$Z_{\text{CPE}} = Q^{-1}(j\omega)^{-n} \quad (2)$$

where  $Q$  = CPE constant,  $n$  = CPE exponent,  $j = (-1)^{1/2}$  is an imaginary number,  $\omega$  = angular frequency which is given by  $\omega = 2\pi f$  where  $f$  = frequency in Hz. Table 1 gives the electrochemical parameters and shows that FE extracts increased the size of  $R_{ct}$  which corresponds to the increase in the size of the semicircle previously mentioned. The addition of FE extracts is also responsible to the decrease in the double layer capacitance ( $Q_{dl}$ ). The observed decrease in the size of  $Q_{dl}$  which results from a decrease in the dielectric constant and/or increase in the double layer thickness can be attributed to the adsorption of the plant extract onto the metal/electrolyte interface.

The inhibition efficiency  $IE_R\%$  was quantified from the impedance data by comparing the values of the charge transfer resistance in the absence ( $R_{ct,bl}$ ) and presence of inhibitor ( $R_{ct,inh}$ ) as follows

$$IE_R\% = \left( \frac{R_{ct,inh} - R_{ct,bl}}{R_{ct,inh}} \right) \times 100. \quad (3)$$

Where  $R_{ct,bl}$  and  $R_{ct,inh}$  are the charge transfer resistance values in the absence and presence of the inhibitor respectively.

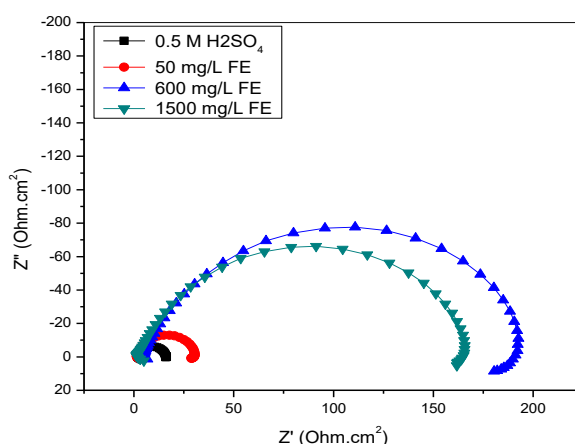


**Figure 4.** Electrochemical impedance spectra of mild steel in 0.5 M  $H_2SO_4$  solution without and with FE extract

**Table 1.** Impedance Results for mild steel Corrosion in 0.5 M  $H_2SO_4$  without and with FE extract.

| System (mg/L)   | $R_{ct}(\Omega cm^2)$ | $Q_{dl}(\mu\Omega^{-1} S^n cm^{-2}) \times 10^{-4}$ | $n$    | $IE_R\%$ |
|-----------------|-----------------------|-----------------------------------------------------|--------|----------|
| $H_2SO_4$ blank | 13.9                  | 3.63                                                | 0.9673 |          |
| FE 50 mg/L      | 59.0                  | 1.07                                                | 0.9242 | 76.5     |
| FE 600 mg/L     | 190.4                 | 0.48                                                | 0.8396 | 91.7     |
| FE 1500 mg/L    | 166.8                 | 0.42                                                | 0.8251 | 92.7     |

Potentiodynamic polarization measurements were undertaken to distinguish the effects on FE extracts on the anodic dissolution of the metal and cathodic reduction of the hydrogen ion.

Typical potential polarization curves for mild steel corrosion in 0.5  $H_2SO_4$  in the presence and absence of FE extracts are shown in Figure 5 while the electrochemical parameters derived from the potentiodynamic polarization experiment are shown in Table 2.

From table 2, the addition of the FE extracts can be seen to affect the anodic dissolution as well as the cathodic reduction partial reactions, shifting the corrosion potential ( $E_{corr}$ ) slightly towards more negative (cathodic) values and reducing both the anodic and cathodic densities and the corresponding current density ( $i_{corr}$ ). From this result, it is clear that the FE extract functioned as mixed type corrosion inhibitor for mild steel in 0.5 M  $H_2SO_4$  solution.

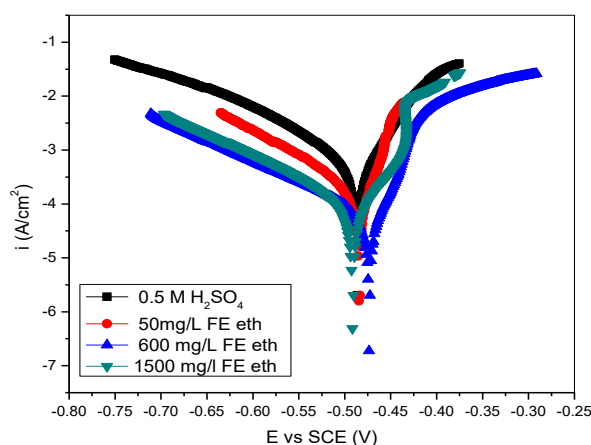


**Figure 5.** Potentiodynamic polarization curves for mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution without and with FE extracts.

**Table 2.** Potentiodynamic polarization parameters for mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> with and without FE extract.

| System (mg/L)                              | E <sub>corr</sub> (mV vs SCE) | i <sub>corr</sub> (μA/cm <sup>2</sup> ) | IE <sub>P</sub> % |
|--------------------------------------------|-------------------------------|-----------------------------------------|-------------------|
| 0.5 M H <sub>2</sub> SO <sub>4</sub> blank | -486.3                        | 593.180                                 |                   |
| 50 mg/L                                    | -504.9                        | 5.703                                   | 99.0              |
| 600 mg/L                                   | -472.5                        | 2.065                                   | 99.6              |
| 1500 mg/L                                  | -491.6                        | 1.173                                   | 99.8              |

The value of the inhibition efficiency from the potentiodynamic polarization measurements can be calculated from the values of the corrosion current densities in the absence  $i_{\text{corr,bl}}$  and the presence  $i_{\text{corr,inh}}$  as follows;

$$\text{IE}_P\% = \left(1 - \frac{i_{\text{corr,inh}}}{i_{\text{corr,bl}}}\right) \times 100. \quad (4)$$

where  $i_{\text{corr,bl}}$  and  $i_{\text{corr,inh}}$  are the corrosion current densities without and with the inhibitor.

**Adsorption considerations:** The inhibitive action of organic components in plant extracts is usually attributed to the adsorption of the active components on the metal surface. The adsorbed layer acts as a barrier preventing both mass and charge transfer. Our impedance data provided direct evidence of the adsorption of the organic matter on the metal surface. Further adsorption characterization can be obtained by considering adsorption isotherms. The fraction of the surface covered by the adsorbed specie  $\theta$ , shows the effectiveness of the adsorbed specie and is directly proportional to the inhibition efficiency IE. the surface coverage  $\theta$  is calculated from the inhibition efficiency as follows;

$$\theta = \text{IE}/100. [32] \quad (5)$$

Adsorption isotherm that describe the behavior of the adsorbed specie compares the value of  $\theta$  with different concentrations of the adsorbed organic matter as determined from the gravimetric measurement after 24 h of immersion. Different adsorption isotherms were tried but the Langmuir adsorption isotherm was observed to fit best to the experimental data. Figure 6 shows the Langmuir adsorption isotherm for FE extract on mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

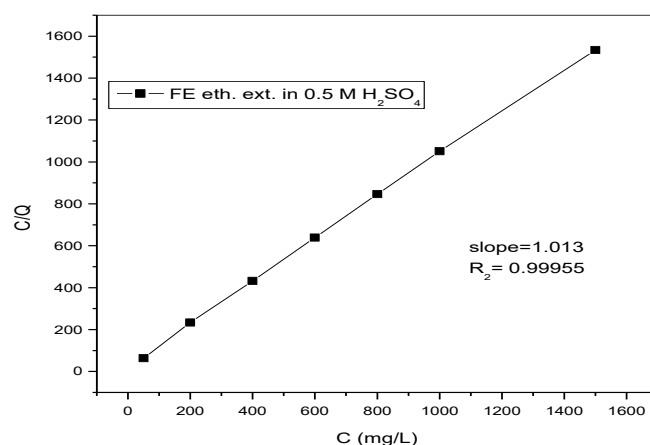


**Figure 6.** Langmuir adsorption isotherm for FE extracts on mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

The expression for the Langmuir adsorption model can be written as follows

$$\text{Log}(C/\theta) = \text{log}C - \text{log}K_{\text{ads.}}, \quad (6)$$

where  $C$  is the concentration of the inhibitor in the electrolyte,  $\theta$  is the degree of surface coverage of the inhibitor, and  $k_{\text{ads}}$  is the equilibrium constant. From Figure 6 it is clear that the values of slope (1.013) and  $R^2$  obtained (0.99955) are very close to unity indicating that there is a strong adherence of the inhibitor adsorption to the assumptions establishing Langmuir adsorption isotherm. The deviation of the slope from the expected value of unity may be attributed to the interactions between adsorbed species on the metal surface as well as changes in the adsorption heat with increasing surface coverage. The fitting of the data to the Langmuir adsorption isotherm confirms that the extract specie adsorbed on the metal surface.

**Fourier Transform Infrared Spectroscopy:** The FTIR spectra for FE powder before extraction, for FE powder after extraction in ethanol as well as scrapings from the inhibitor films on the surface of the mild steel specimen after 3 h hours of immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 1500 mg/L FE extract are presented in Figure 7. The multiplicity of peaks in the spectra for FE powder indicates the presence of complex organic compounds in the plant material. It can be observed from the curves that nearly all the peaks observed for FE powder before extraction are retained after extraction showing that not all the functional groups were lost through extraction. Again it is observed that almost all the peaks observed for FE powder are again observed on the films from the mild steel surface after immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> which means that most of the functional group participated in the adsorption process. The peaks with subdued intensities in the adsorbed surface films are (C-O) single bands around (1200cm<sup>-1</sup>-1300cm<sup>-1</sup>), (C=O) stretching around (1600cm<sup>-1</sup>-1800cm<sup>-1</sup>), (O-H) bands around (3300-3600 cm<sup>-1</sup>) which suggest that these functional groups are directly involved in the metal protection.

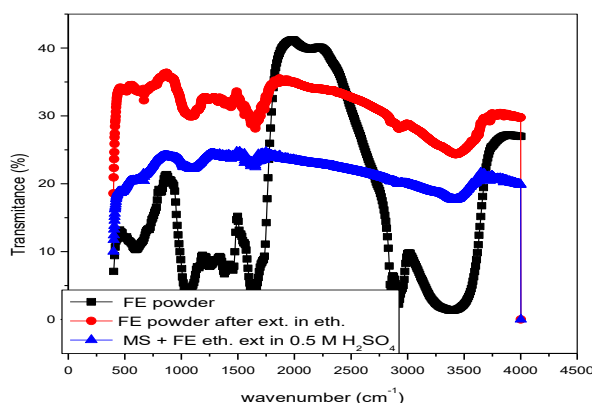


**Figure 7.** FTIR spectra of FE powder before and after extraction as well as that of surface film on mild steel specimen immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing FE extract.

**Effect of temperature;** To study the effect of temperature on the corrosion process, weight loss experiments were performed at 30, 40, 50 and 60°C in the uninhibited and in the inhibited solutions containing 50, 200, 400, 600, 800, 1000 and 1500 mg/L FE extract for 3 h of immersion. The choice of these 7 concentrations was to reflect the effect of temperature over a wide range of surface coverage. The relationship between inhibition efficiency and temperature is represented in Figure 8 while the effect of temperature on corrosion rate is shown in Figure 9.

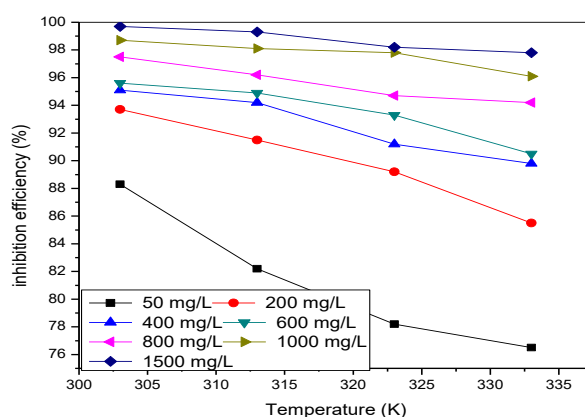


**Figure 8.** Effect of temperature on the inhibition efficiency (%) of FE, ethanol extract for mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub>

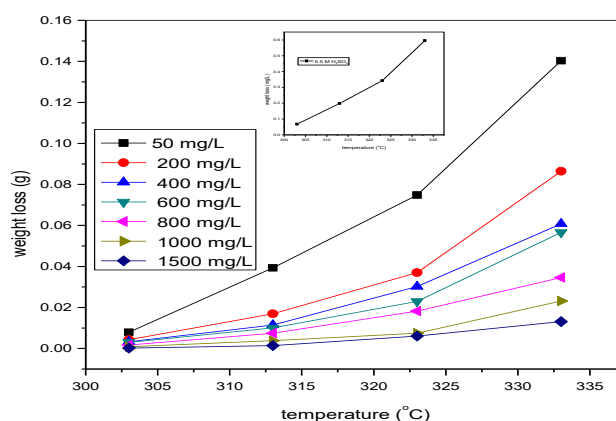


**Figure 9.** Effect of temperature on the corrosion rates of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> without (insert) and with FE extracts.

The results in Figure 8 indicate that inhibition efficiency decreased with increase in temperature for FE extract which is the trend suspected for physical adsorption mechanism, it is also clear from Figure 8 that high inhibition efficiency was maintained at all the temperatures studied. The results in Figure 9 indicate that corrosion rate in both inhibited and uninhibited systems increases with increase in temperature. The Arrhenius equation below was used to determine the activation energy [33, 34].

$$\text{Log } \frac{CR_2}{CR_1} = -\frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right). \quad (7)$$

Where  $CR_1$  and  $CR_2$  are the corrosion rates of mild steel at the temperatures  $T_1$  (303 K) and  $T_2$  (333), respectively,  $E_a$  is the activation energy and  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). Values of  $E_a$  calculated from Equation (7) are presented in Table 3. From the result, it can be seen that the obtained  $E_a$  is higher than that observed in the uninhibited acid. The activation energies obtained in Table 3 are within the range suspected for physical adsorption mechanism. Hence the adsorption of ethanol extract of FE is suspected to be consistent with physical adsorption.

**Table 3.** Activation Energies for Mild Steel corrosion in 0.5 M  $\text{H}_2\text{SO}_4$  without and with FE extracts

| System (mg/L)                 | $E_a$ (kJ/mol) |
|-------------------------------|----------------|
| 0.5 M $\text{H}_2\text{SO}_4$ | 60.2           |
| 50                            | 79.7           |
| 200                           | 83.2           |
| 400                           | 80.8           |
| 600                           | 81.4           |
| 800                           | 83.5           |
| 1000                          | 90.1           |
| 1500                          | 115.9          |

**Computational consideration:** Inhibiting action of plant extracts is known to occur via adsorption of the phytochemical constituents of the plant material on the surface of the corroding metal surface. Precise experimental determination of the contributions of the individual constituents to the overall inhibiting process was hindered by the complex nature of the plant material. Hence, we rely on quantum chemical computation and molecular dynamic simulation to ascertain the individual contributions of the phytochemicals to the overall inhibition process. The results of the phytochemical screening of *Funtumia elastica* was described elsewhere [35]. the selected extract constituents are conessine, and ascorbic acid. Quantum chemical computations and molecular dynamic simulations were used to describe the electronic structures of these constituents with a view to establishing the active sites as well as reactivity of the molecules. The simulations were performed by means of density functional theory (DFT) electronic structure program DMol<sup>3</sup> using a Mulliken population analysis. [36,37]. Electronic parameters for the simulation include restricted spin polarization using DND basis set and Perdew-Wang(PW) local correlation density functional. Details of the computation methods are presented in [38, 39]. Figure 10 represents the electronic properties of conessine, 10(a) represents the optimized structure 10(b) shows the highest occupied molecular orbital 10(c) represents the lowest unoccupied molecular orbital (LUMO) 10(d) is the total electron density 10(e) shows the center for electrophilic attack and 8(f) is the centre for nucleophilic attack. From Figure 10(d), the electron density can be seen to saturate all around the molecule which facilitates flat lying adsorption position. The HOMO is the orbital that acts as an electron donor and they represent the active site of the constituents. The position of LUMO represents the vacant orbital that acts as electron acceptor since, it is the innermost (lowest energy) orbital that is vacant ready to accept electrons, the LUMO orbital can accept electrons in the d-orbital of the metal using anti-bonding orbitals to form feedback bond [40]. Similar structures for ascorbic acid are shown in Figure 11.

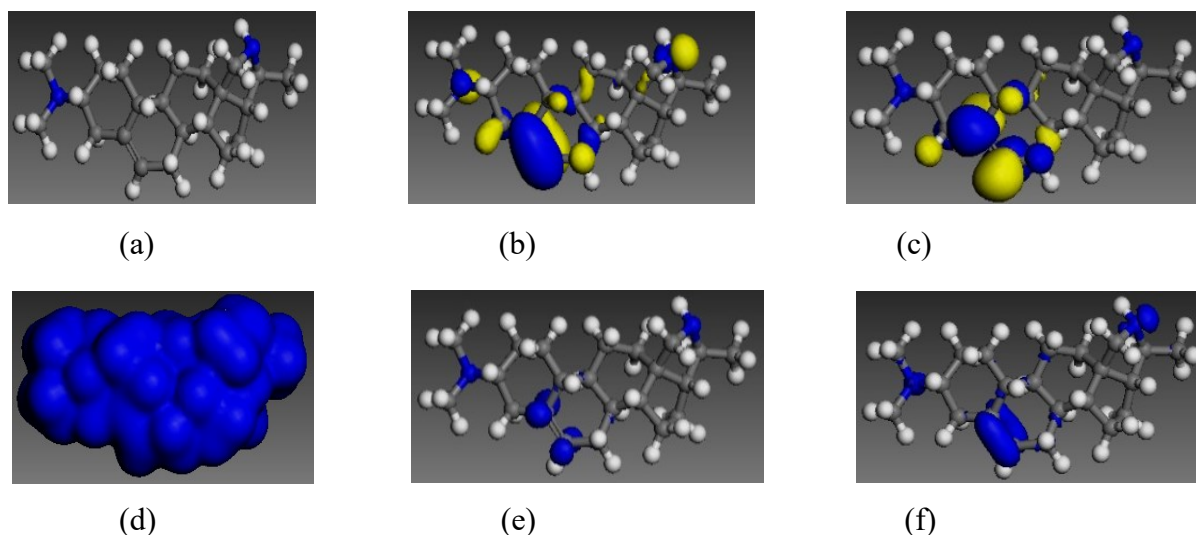


**Figure 10.** Electronic properties of conessine (a) optimized structure (b) HOMO orbital (c) LUMO orbital (d) total electron density (d) center for electrophilic attack and (e) center for nucleophilic attack. Atom legend: white = H; gray = C; red = O; blue = N. The blue and yellow isosurfaces depict the electron density difference: the blue regions show electron accumulation while the yellow regions show electron loss.

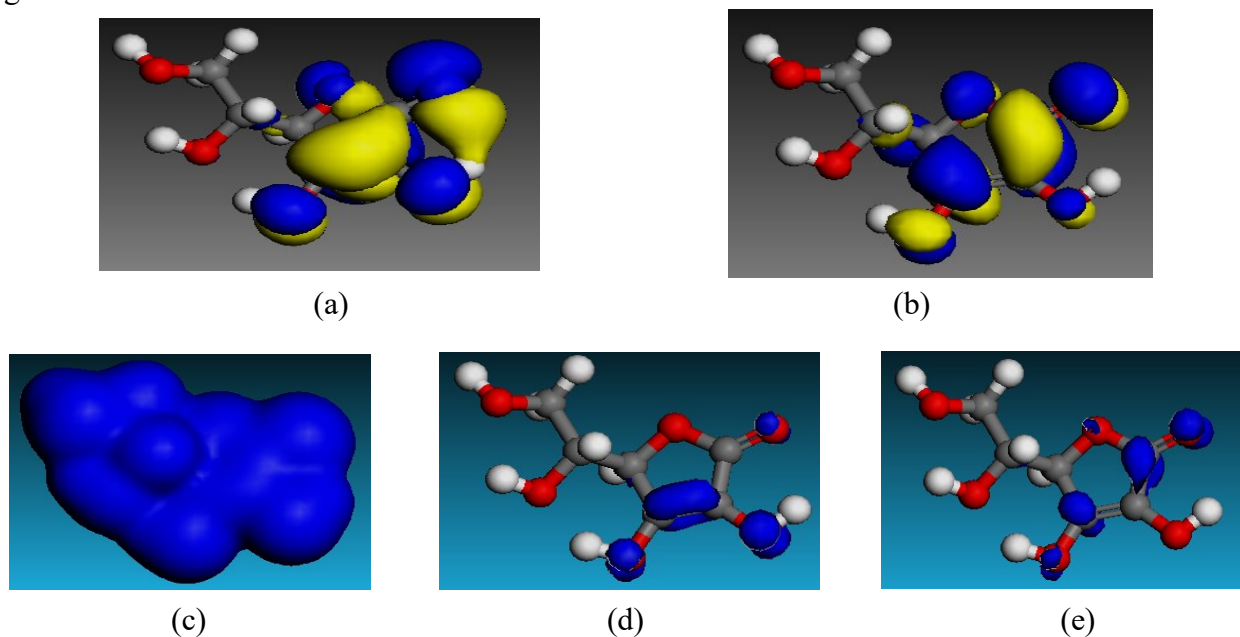


**Figure 11.** Electronic properties of ascorbic acid (a) HOMO orbital (b) LUMO orbital (c) total electron density (d) center for electrophilic attack and (e) center for nucleophilic attack. Atom legend: white = H; gray = C; red = O; blue = N. The blue and yellow isosurfaces depict the electron density difference: the blue regions show electron accumulation while the yellow regions show electron loss.

Table 4, shows the quantum chemical parameters related to the molecular electronic structures of the most stable conformation molecules. The energy gap  $\Delta E$  is given by  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ .

A high value of  $E_{\text{HOMO}}$  is an indication that the molecule is ready to donate electrons to the metal with vacant molecular orbitals. Low values of  $\Delta E$  will favor high inhibition efficiency since the energy to remove an electron from the last occupied orbital is reduced resulting in higher inhibition efficiency [41-43]. The HOMO and LUMO energies are directly related to the ionization potential (I) and electron affinity (A), respectively as follows

$$I = -E_{\text{HOMO}}$$

$$A = -E_{\text{LUMO}}$$

Electron charge transfer, ( $\Delta N$ ) from Lewis base (the inhibitor) to Lewis acid (the metal surface) was quantified using the equation below

$$\Delta N = \frac{X_m - X_i}{2(\eta_m + \eta_i)} \quad (8)$$

Where  $X_m$  and  $X_i$  are the absolute electronegativity of the metal and inhibitor molecule, respectively,  $\eta_m$  and  $\eta_i$  are the absolute hardness of the metal and inhibitor molecule respectively. The  $\Delta N$  values presented in Table 4 were calculated using theoretical values of 7eV/mol and 0 eV/mol for  $X_m$  and  $\eta_m$  respectively [44].  $\Delta N$  values have been reported to increase with increase in inhibition efficiency [45]. The values of the computed chemical parameters presented in Table 4 suggest that the reactivity order of the selected molecules in aqueous phase is conessine > ascorbic acid.

**Table 4.** Calculated quantum chemical properties for the most stable configuration of conessine and ascorbic acid

| Property                     | Conessine | ascorbic acid |
|------------------------------|-----------|---------------|
| $E_{HOMO}$ (Ev)              | -4.652    | -6.031        |
| $E_{LUMO}$ (Ev)              | -0.284    | -2.294        |
| $E_{LUMO-HOMO}$              | 4.368     | 3.737         |
| Adsorption energy (Kcal/mol) | -171.1    | -30.3         |
| $X$                          | 2.468     | 4.163         |
| $\eta$                       | 2.184     | 1.869         |
| $\Delta N$                   | 1.038     | 0.759         |

From the calculated values it is clear that all the molecules have comparable values of  $E_{HOMO}$ , which may be attributed to the presence of the functional group comprising the HOMO being present in all the chosen constituents. The comparable  $E_{HOMO}$  values are indications that the constituents adsorbed on the metal surface. The adsorption strength of the molecules can also be determined by molecular size in addition to the electronic structure calculations already done. Adsorption of the different molecules on the metal surface was analyzed at a molecular level by molecular dynamics (MD) simulations, using Forcite quench molecular dynamics to sample some different low energy configurations of the molecule and identify the minima [46,47]. Calculations were done using COMPASS force field and the Smart algorithm, using a simulation box 30 Å x 25 Å x 29 Å with periodic boundary conditions to model a representative part of the interface, not containing boundary defects. The box was made up of Fe slab, cleaved along the Fe (110) plane and a vacuum layer of 20 Å heights. The geometry of the bottom layer of the slab was constrained to the bulk positions, whereas other degrees of freedom were relaxed before optimizing the Fe(110) surface which was subsequently enlarged into a 12 x 8 supercell. The system was quenched every 250 steps. Optimized structures of the inhibitor constituents were used for the simulation.

Figure 12 (a-b) shows representative snapshots of the side view of the most stable configurations for single molecules of conessine and ascorbic acid respectively on the Fe(110) surface from our simulation while Figures 13 (a-b) shows the top view versions for conessine, and ascorbic acid. Each molecule can be seen to maintain a flat lying adsorption orientation on the surface of the metal as expected from the delocalization of the electron density around the molecules. This orientation can be said to maximize contact between the metal surface and the inhibitor molecule. To quantitatively determine the interaction between the metal surface and the inhibitor molecule the adsorption energies ( $E_{ads}$ ) were computed using the relationship below

$$E_{ads} = E_{total} - E_{mol} + E_{Fe}. \quad (9)$$

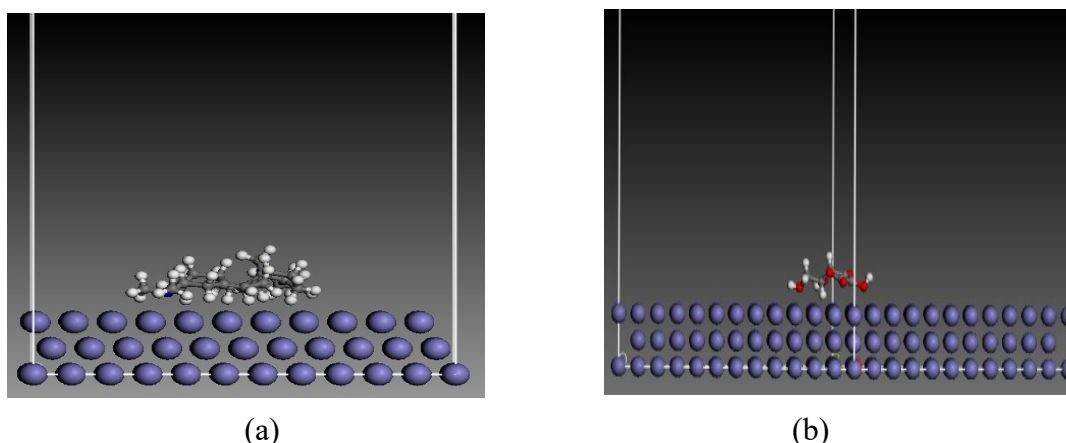


**Figure 12.** Representative snapshots of (a) conessine and (b) ascorbic acid adsorbed on the Fe (110) molecule

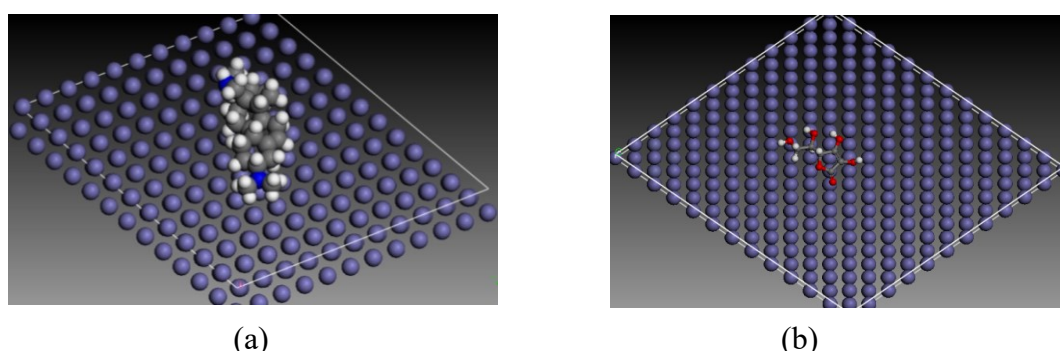


**Figure 13.** Top view of Representative snapshots from molecular dynamics models of: (a) conessine and (b) ascorbic acid adsorbed on the Fe (110) molecule

The adsorption energies of the constituents are presented in Table 3, all the adsorption energies are negative corresponding to a stable adsorption structures.  $E_{Fe}$ ,  $E_{mol}$  and  $E_{ads}$  correspond respectively to the Fe (110) slab, adsorbed mol/Fe(110) coupled in the gas phase and the total energies of the molecule. The total energies were obtained by averaging the energies of the five most stable adsorption configurations. The obtained values of  $E_{ads}$  values -171.1 for conessine, and -30 for ascorbic acid are all negative indicating stable adsorption structures. The trend in adsorption energy correspond to the trend in molecular size (conessine > ascorbic acid) showing that the larger molecules adsorb better than smaller ones.

## CONCLUSION

From the results of this research, it has been established that ethanol extract of *Funtumia elastica* inhibit the corrosion of mild steel in 0.5 M  $H_2SO_4$ . Gravimetric experiment showed that FE maintained high inhibition efficiency even at prolonged exposure time. Polarization studies revealed that the plant extract functioned as a mixed type corrosion inhibitor for mild steel in 0.5 M  $H_2SO_4$  solution. Impedance results revealed that the corrosion inhibition of FE was achieved by the adsorption of the extract constituents on the surface of the mild steel. Effect of temperature showed that FE maintained high corrosion inhibition even at 333°C. Density functional theory (DFT) – based quantum chemical computation of parameters associated with the electronic structures of some selected extract constituents confirmed the extracts inherent affinity towards adsorption on the mild steel surface with conessine showing the greater adsorption strength. The results of this research revealed that FE ethanol extract is an excellent corrosion inhibitor for mild steel in 0.5 M  $H_2SO_4$ .

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