Jatropha podagrica stem bark extract as a novel green corrosion inhibitor for carbon steel in acid medium: A combined experimental and computational explorations

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Abstract
The inhibition efficacy of a novel green corrosion inhibitor based on Jatropha podagrica stem bark extract (JPSE) toward carbon steel (CS) corrosion in 0.5 M H₂SO₄ solution was explored by integrated experimental and computational studies. The inhibition behavior was probed using weight loss analysis, potentiodynamic polarization (PDP) test, electrochemical impedance spectroscopy (EIS) and surface analysis techniques. In addition, the adsorption process between JPSE compounds and iron atom was theoretically examined by using quantum chemical calculations and molecular dynamics (MD) simulations. The experimental results revealed that 600 mg L⁻¹ JPSE protected the CS surface by ~87%. The polarization tests revealed that the JPSE acted as a mixed type inhibitor with dominant effect on the cathodic reaction restriction. The EIS analysis showed that the increase of JPSE concentration led to the significant increment of charge transfer resistance. Surface analysis via SEM clearly proved that JPSE adsorption on the CS surface remarkably reduced its dissolution rate and resulted in a smooth morphology. UV–visible analysis evidenced the formation of a complex between the functional groups of the considered inhibitor and metal ions. The theoretical results demonstrated the adsorption of JPSE constituents on the CS substrate in parallel mode.

Keywords: Green corrosion inhibitor; Jatropha podagrica stem extract; Electrochemical techniques; Molecular dynamics; Carbon steel.
1. Introduction

Carbon steel (CS) has substantial industrial and economic importance due to its promising mechanical properties and relatively low price [1]. The corrosion of metallic materials affects the industrial sector and can cost billions of dollars each year [2]. In the course of industrial operations, CS and generally ferrous alloys are aggressively attacked by strong acid solutions i.e., HCl, H2SO4 and HNO3, which causes loss of metallic structures as a result of corrosion. Several techniques including cathodic/anodic protection, electroplating, painting and the use of inhibitors have been engaged to combat this scourge. The use of corrosion inhibitors is widely regarded as one of the most practical and sustainable strategy to mitigate the corrosion phenomenon. Organic compounds containing heteroatoms (i.e. oxygen, sulfur, nitrogen), conjugated double bonds, and/or polar functional groups generally exhibit favorable anticorrosion activity, so they can always be used as inhibitor for metals corrosion in aggressive medium [3,4]. However, some of these compounds are expensive and provide high risks to humans and the environment. In recent times, corrosion scientists are showing great interest in the use of green inhibitors, namely, extracts and essential oils of medicinal and aromatic plants [5]. The choice of these green inhibitors basically resides in their non-toxicity, low cost, renewability and a high inhibition performance even at low concentrations [6]. The inhibitory effect of these inhibitors is often ascribed to the richness of organic compounds that can be adsorbed on the metal surface, which leads to the formation of a defensive layer and therefore effectively retard the corrosion process [7].

In this regard, *Jatropha podagrica* was employed as a new green source of corrosion inhibitors for CS in acidic medium. *J. podagrica* is a succulent shrub that is widely distributed in Africa, Asia and Latin America. The extracts of different parts of this plant have been reported to exhibit wide range of biological activities including antibacterial, antitumor, antioxidant and antimicrobial [8,9]. Having been utilized successfully for medicinal purposes, it is imperative to consider *Jatropha podagrica* extracts as anticorrosion agent. According to literature, gallic acid, fraxetin, and tomentin are some of the main components present in the stem bark extract of *Jatropha podagrica* [10]. All these compounds are made up of oxygen heteroatom and aromatic loops that can chelate with vacant 3d orbital of metal cations and thus served as potent inhibitors in corrosive media. To the best of our knowledge, the use of *Jatropha podagrica* stem bark extract against CS corrosion in acidic solution has not been documented previously.

The current research is focused on evaluating the corrosion inhibition performance of the *Jatropha podagrica* stem bark extract (JPSE) on CS in 0.5 M H2SO4 solution. The inhibition behavior was probed using weight loss (WL) analysis, potentiodynamic polarization (PDP) tests and electrochemical impedance spectroscopy (EIS). The adsorption properties of the tested inhibitor were examined via scanning electron microscopy (SEM) and UV-visible analysis. Besides, the theoretical methods based on quantum chemical computations and molecular dynamics (MD) simulations were applied to gain detailed insights regarding the electronic-structure properties and interfacial interactions of the inhibitor molecules with Fe ions on the CS surface.
2. Materials and Methods

2.1. Specimens and corrodenent

Identical CS specimens with dimension of 3.0 cm x 2.9 cm x 1.2 cm were cut out from CS sheet with chemical composition (wt%): C (0.19), Mn (0.94), P (0.002), Si (0.06), Cr (0.054), Cu (0.022), Ti (0.002), Ni (0.015), Al (0.023), and Fe (remainder). Before the experiments, the exposed surfaces of the specimens were polished with different grades sandpapers (600, 800 and 1000), washed with distilled water, degreased with ethanol, dried using hot air blower and finally kept properly in a desiccator for subsequent use. The corrosive medium (0.5 M H₂SO₄) was prepared by diluting analytical grade sulfuric acid (98%; purchased from E. Merck) with distilled water.

2.2. Preparation of extract

*J. podagrica* stem barks were collected from Gombe State, Nigeria. The barks were identified and authenticated at the herbarium unit of Plant Biology Department, Bayero University, Kano. The full details on the preparation and extraction procedure of the sample have been earlier reported [10] and similar protocol was adopted in our study. Briefly, 100 g of *J. podagrica* stem bark powder was added to 500 mL of methanol and then agitated for two weeks at room temperature. The extract solution was then concentrated under vacuum at 40°C using a rotary evaporator. Thereafter, 150, 300, 450 and 600 mg of the obtained extract powder were added to 0.5 M H₂SO₄ solution and agitated to obtain a clear solution. The chemical structures of the main components of JPSE are disclosed in Fig. 1.

![Gallic acid](image1)

![Fraxetin](image2)

![Tomentin](image3)

**Fig. 1.** Chemical structures of some of the main constituents of JPSE
2.3. Corrosion studies

2.3.1. Weight loss measurements

The weight-loss experiments were carried out under static conditions. Beakers (150 mL capacity) were filled with 100 mL of test solutions (0.5 M H₂SO₄ solution without and with different concentrations of inhibitor). They were then placed in a thermostatically controlled water bath maintained at studied temperatures (303, 313, 323 and 333K). The polished CS specimens (3.0 cm × 2.9cm × 1.2 cm) in triplicate were dipped in the test medium for 9 h. The concentrations of inhibitor studied were 150, 300, 450 and 600 mg L⁻¹. After 9 h of exposure, the specimens were retrieved and treated appropriately. The corrosion rate ($C_R$) of the immersed specimen was computed using the weight loss data as per Equation 1:

$$C_R = \frac{W_o - W_i}{St}$$  (1)

where S denotes the surface area of CS specimen (cm²); t represents the exposure time (h); $W_o$ and $W_i$ represent the weight loss (g) before and after immersion in the test solution. Furthermore, the corrosion inhibition efficiency was calculated using Equation 2:

$$\%IE_{WL} = \frac{C_R^0 - C_R^i}{C_R^0} \times 100$$  (2)

where $C_R^0$ and $C_R^i$ are the corrosion rate (g. cm⁻² h⁻¹) of the uninhibited and inhibited specimens, respectively.

2.3.2. Electrochemical assessments

The electrochemical analyses were accomplished at 30 °C using a G-300 Gamry potentiostat/galvanostat driven by the Gamry Echem Analyst (version 5.0) software. A conventional three-electrode cell consisting of working electrode (CS specimen), an auxiliary electrode (platinum foil) and reference electrode(saturated caramel electrode) was employed for all electrochemical experiments. The CS surface have been prepared by abrading using various sandpapers (600-1000), washing by distilled water, degreasing by acetone, and finally drying. Prior to each electrochemical tests, the CS working electrode was dipped in corrosive solution for 30 min to reach a steady value of open-circuit potential (OCP). The potentiodynamic polarization (PDP) curves were obtained in the potential range and sweep rate of −250 to +250mV against stable OCP and 1 mV s⁻¹, respectively. The EIS tests were performed in the frequency scope of 0.01 Hz to 100kHz with a perturbation of 10 mV using an AC signal at OCP. The Gamry Echem Analyst software was used for the fitting and analysis of the data generated from EIS and PDP measurements.

2.4. Surface and solution analyses

The surface morphology of the cleaned CS specimens before and after 9 h of immersion in 0.5 M H₂SO₄ solution without and with different concentration of JPSE at 30 °C was observed using a scanning...
electron microscope (Phenomn Pro X) at 500x magnification. Meanwhile, UV–visible analysis was performed to gain clues into the mechanism of interaction between the inhibitor molecules and the steel surface. In view of this, the absorption profiles of 0.5 M H$_2$SO$_4$ solution + JPSE before and after CS specimen immersion were recorded between 200-750 nm using Perkin Elmer UV–visible spectrophotometer (Labda 35) with a scan speed of 960 nm min$^{-1}$.

2.5. Computational details

2.5.1. Quantum chemical studies

The geometric and electronic properties of the major JPSE constituents (gallic acid, fraxetin, and tomentin) were explored using the DFT/B3LYP/DND level of theory as implemented in Materials Studio (version 8.0) software. The DFT-optimized geometries of the compounds were then adopted for analysis of electronic properties, which include electron density distribution, Fukui indices as well as energies linked to frontier molecular orbitals (i.e., energy of highest occupied molecular orbital, $E_{HOMO}$, energy of lowest unoccupied molecular orbital, $E_{LUMO}$, and energy gap, $\Delta E = E_{LUMO} - E_{HOMO}$). The frontier molecular orbital energies were subsequently employed for evaluating the reactivity of the selected compounds in terms of global reactivity descriptors including chemical hardness ($\eta$), electronegativity ($\chi$) and fraction of electronic charges exchanged at interface ($\Delta N$). These global properties were in turn dependent on ionization energy ($I = -E_{HOMO}$) and electronic affinity ($A = -E_{LUMO}$) [11]:

$$\eta = \frac{I - A}{2} = \frac{E_{LUMO} - E_{HOMO}}{2} = \frac{1}{2} \Delta E$$ \hspace{1cm} (3)

$$\chi = \frac{I + A}{2} = -\frac{E_{HOMO} + E_{LUMO}}{2}$$ \hspace{1cm} (4)

The fraction of transferred electrons ($\Delta N$) was assessed using Equation 5 [12]:

$$\Delta N = \frac{\Phi - \chi_{\text{inhibitor}}}{2\eta_{\text{inhibitor}}}$$ \hspace{1cm} (5)

For the computation of $\Delta N$, the iron work function (i.e., $\Phi = 4.82$) was utilized. The local reactivity of the target molecules were characterized by the analysis of Fukui functions on the basis of the following formula [13]:

$$f_k^+ = q_k(N + 1) - q_k(N)$$ \hspace{1cm} (6)

$$f_k^- = q_k(N) - q_k(N - 1)$$ \hspace{1cm} (7)

where $f_k^+$ and $f_k^-$ reflect the nucleophilic and electrophilic affinity, respectively; $q_k$ denotes the electronic population of an atomic site within a molecule in its anionic ($N + 1$), neutral ($N$), or cationic ($N - 1$) state. The analysis of Fukui functions was accomplished using DFT calculations executed by means of DMol$^3$ module of Materials Studio software (version 8.0).
2.5.2. Molecular dynamics simulation
The interactions between investigated inhibitor molecules and CS surface were probed with MD method using for cite module of the Materials Studio 8.0 software. Since Fe (110) plane has extremely packed structure and higher stabilization energy [14], it has been adopted to represent CS substrate. The COMPASS force field and the NVE canonical ensemble were adopted for all simulations. During the simulation protocol, all the atoms in the Fe (110) surface were fixed and inhibitor molecules are allowed to interact freely with the metal surface. The simulations were accomplished at 303 K using time step of 1 fs and simulation time of 500 ps, which is controlled using the Smart algorithm [15]. The adsorption and the binding energies \( E_{\text{Binding}} = -E_{\text{adsorption}} \) were estimated when the system attains the equilibrium state as per Equation8 [16]:

\[
E_{\text{ads}} = E_{\text{Total}} - (E_{\text{surface+solution}} + E_{\text{inhibitor}})
\]

where \( E_{\text{Total}} \) expresses the total potential energy of the entire system, \( E_{\text{surface+solution}} \) reflects the energy of Fe (110) and solution in the absence of inhibitor, and the term \( E_{\text{inhibitor}} \) illustrates the energy of isolated inhibitor molecule.

3. Results and Discussion
3.1. Weight loss analysis
Table 1 disclose the numerical values of corrosion rate (\( C_R \)) and inhibition efficiency (%IE) for CS at varying concentrations of JPSE. The inspection of the data revealed that by raising the concentration of the inhibitor, the corrosion rate of the CS was substantially suppressed while the inhibition performance was improved. This phenomenon was attributed to the adsorption of active components of JPSE on the CS surface. Meanwhile, the highest inhibition performance of 90.40% was obtained when the test solution was pretreated with 600 mg L\(^{-1}\) of the tested extract, indicating a significant degree of CS surface protection against the corrosive medium. Table 1 also displays the corrosion parameters under different temperature conditions. It was observed that the \( C_R \) appreciably increased with increasing the temperature. This implies that the steel dissolution rate was amplified at elevated temperatures. In addition, the \( C_R \) for the inhibited specimens were notably lower than those of the uninhibited specimens, signifying that the inhibitor could effectively reduce the CS dissolution rate.
Table 1. Weight loss parameters of CS in 0.5 M H$_2$SO$_4$ in absence and presence of different concentration of JPSE at different temperatures

<table>
<thead>
<tr>
<th>Conc. (mg L$^{-1}$)</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
<th>333 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_R$ (mg. cm$^{-2}$ h$^{-1}$)</td>
<td>% IE$_{WL}$</td>
<td>$C_R$ (mg. cm$^{-2}$ h$^{-1}$)</td>
<td>% IE$_{WL}$</td>
</tr>
<tr>
<td>Blank</td>
<td>1.98</td>
<td>—</td>
<td>3.65</td>
<td>—</td>
</tr>
<tr>
<td>150</td>
<td>0.91</td>
<td>54.04</td>
<td>1.88</td>
<td>48.49</td>
</tr>
<tr>
<td>300</td>
<td>0.57</td>
<td>71.21</td>
<td>1.30</td>
<td>64.38</td>
</tr>
<tr>
<td>450</td>
<td>0.32</td>
<td>83.83</td>
<td>0.88</td>
<td>75.89</td>
</tr>
<tr>
<td>600</td>
<td>0.19</td>
<td>90.40</td>
<td>0.53</td>
<td>85.47</td>
</tr>
</tbody>
</table>

3.2. Calculation of activation and thermodynamic parameters

The Arrhenius and transition state equations (Equations 9 and 10) were employed to examine the effect of temperature on the corrosion phenomenon of CS in 0.5 M H$_2$SO$_4$ solution [17]:

$$\log C_R = \frac{-E_a}{2.303RT} + \log A$$

(9)

$$\log \left( \frac{C_R}{T} \right) = \left[ \log \left( \frac{R}{Nh} \right) + \frac{\Delta S_a^*}{2.303 R} \right] - \frac{\Delta H_a^*}{2.303 RT}$$

(10)

where $E_a$, $\Delta H_a^*$, $\Delta S_a^*$, N and h denote the activation energy, activation enthalpy, activation entropy, Avogadro's number and Planck's constant, respectively. The Arrhenius and transition state plots for CS corrosion in 0.5 M H$_2$SO$_4$ are presented in Figs. 2-3, and the values of relevant parameters are collected in Table 2.

The results in Table 2 revealed that the estimated values of $E_a$ in the presence of inhibitor are higher than that of the bare acid solution, which can be ascribed to the formation of energy barrier for metallic dissolution process in the presence of inhibiting species [18]. Furthermore, by increasing the JPSE concentration, the $E_a$ increased to higher values, reflecting the decrease in corrosion rate. The positive values of $\Delta H_a^*$ implies that the CS dissolution is an endothermic process. This has also been reported to be reflective of retarded dissolution of metal in inhibitor-bearing solution. The values of $\Delta S^*$ are negative, indicating that the rate controlling step involves association rather than dissociating phenomenon in the formation of activated complex [19]. The change in activation free energy ($\Delta G_a^*$) was calculated using Equation 11:

$$\Delta G_a^* = \Delta H_a^* - T \Delta S_a^*$$

(11)

The values of $\Delta G_a^*$ disclosed in Table 2 are positive indicating that the activated complex is unstable. Furthermore, $\Delta G_a^*$ increases very slightly with rising temperature, implying that thermodynamic favorability of activated complex formation decline with increasing temperature [20].
Fig. 2. Arrhenius plots for CS in 0.5 M H$_2$SO$_4$ at different concentrations of JPSE

Fig. 3. Transition state plots for CS in 0.5 M H$_2$SO$_4$ at different concentrations of JPSE
Table 2. Activation parameters for CS corrosion in 0.5 M H$_2$SO$_4$ in the absence and presence of different concentrations of JPSE

<table>
<thead>
<tr>
<th>Conc. (mg L$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (J mol$^{-1}$K$^{-1}$)</th>
<th>$\Delta G^\circ$ 303 K</th>
<th>$\Delta G^\circ$ 313 K</th>
<th>$\Delta G^\circ$ 323 K</th>
<th>$\Delta G^\circ$ 333 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>46.01</td>
<td>43.36</td>
<td>$-95.93$</td>
<td>29.11</td>
<td>30.07</td>
<td>31.03</td>
<td>31.99</td>
</tr>
<tr>
<td>150</td>
<td>54.02</td>
<td>51.39</td>
<td>$-75.84$</td>
<td>23.03</td>
<td>23.73</td>
<td>24.55</td>
<td>25.30</td>
</tr>
<tr>
<td>300</td>
<td>59.41</td>
<td>56.79</td>
<td>$-61.77$</td>
<td>18.77</td>
<td>19.39</td>
<td>20.00</td>
<td>20.63</td>
</tr>
<tr>
<td>450</td>
<td>66.94</td>
<td>64.33</td>
<td>$-41.35$</td>
<td>12.58</td>
<td>13.00</td>
<td>13.42</td>
<td>13.83</td>
</tr>
<tr>
<td>600</td>
<td>73.72</td>
<td>71.13</td>
<td>$-23.46$</td>
<td>7.18</td>
<td>7.41</td>
<td>7.65</td>
<td>7.88</td>
</tr>
</tbody>
</table>

3.3. Potentiodynamic polarization curves

The polarization curves (Tafel plots) for CS working electrode in 0.5 M H$_2$SO$_4$ in the absence and presence of different concentrations (150–600 mg L$^{-1}$) of the examined inhibitor are displayed in Fig. 4. The values of key electrochemical parameters, including corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), cathodic and anodic Tafel slopes ($\beta_c$ and $\beta_a$) obtained from the Tafel fit extrapolation are listed in Table 3. The inhibition efficiency of JPSE from PDP technique was calculated using Equation 12:

$$\% \text{ I}E_{PDP} = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100$$

where $I_{corr}^0$ and $I_{corr}$ denote the corrosion densities of CS electrode in bare and inhibitor-containing solution, respectively.

It is obvious from the data presented in Table 3 that the corrosion current density ($I_{corr}$) decreases remarkably in the presence of the inhibitor, implying that the active components of JPSE inhibit CS corrosion in 0.5 M H$_2$SO$_4$ solution. It has been established that the shift in the value of corrosion potential ($E_{corr}$) is a key parameter for verifying whether the inhibitive effect is cathodic or anodic biased. Generally, inhibitors of corrosion can be regarded as cathodic or anodic type if the displacement value of $E_{corr}$ is greater than 85 mV with reference to the value obtained for the uninhibited acid solution [21]. In the current study, the maximum shift in the $E_{corr}$ value of the inhibitor containing system relative to the $E_{corr}$ of the blank, was 29.5 mV, intimating that the tested JPSE behave as mixed-type inhibitor [22]. That is, it inhibits both the anodic metallic dissolution and cathodic hydrogen evolution reaction [23]. However, the higher values of $\beta_c$ compared to the values of $\beta_a$ signifies predominant cathodic behavior and thus, the inhibitor will have more influence on the cathodic reaction sites [24]. Further inspection of the data shown in Table 3 reveals that the increase in inhibitor concentration was accompanied by a decrease in current density ($I_{corr}$), which in turn leads to higher inhibition performance. This is attributed to the formation of defensive layer of inhibitor on CS surface, thereby reducing the corrosion current density by blocking the available corrosion reaction active sites [25].
**Fig. 4.** Tafel polarization curves for CS in 0.5 M H₂SO₄ without and with different concentrations of the inhibitor.

**Table 3.** Electrochemical polarization parameters for CS in 0.5 M H₂SO₄ in the absence and presence of different concentrations of JPSE.

<table>
<thead>
<tr>
<th>Conc. (mg L⁻¹)</th>
<th>$\Delta E_{corr}$ (mV)</th>
<th>$I_{corr}$ (mA cm⁻²)</th>
<th>$R_p$ (Ohm cm⁻²)</th>
<th>$\beta_a$ (mV dec⁻¹)</th>
<th>$\beta_c$ (mV dec⁻¹)</th>
<th>% IE_{PDP}</th>
</tr>
</thead>
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<tr>
<td>Blank</td>
<td>469.8</td>
<td>8.45</td>
<td>1.10</td>
<td>80.6</td>
<td>164.0</td>
<td>—</td>
</tr>
<tr>
<td>150</td>
<td>499.3</td>
<td>3.46</td>
<td>3.91</td>
<td>102.3</td>
<td>180.1</td>
<td>59.10</td>
</tr>
<tr>
<td>300</td>
<td>478.5</td>
<td>2.62</td>
<td>3.12</td>
<td>90.7</td>
<td>179.8</td>
<td>68.99</td>
</tr>
<tr>
<td>450</td>
<td>489.4</td>
<td>1.84</td>
<td>3.36</td>
<td>94.4</td>
<td>170.6</td>
<td>78.22</td>
</tr>
<tr>
<td>600</td>
<td>492.1</td>
<td>1.11</td>
<td>3.47</td>
<td>92.8</td>
<td>169.9</td>
<td>86.86</td>
</tr>
</tbody>
</table>

**3.4. Electrochemical impedance spectroscopy (EIS) technique**

EIS measurements for CS corrosion in 0.5 M H₂SO₄ in the absence and presence of different concentrations of JPSE were performed to gain more insights about the kinetics of the electrode processes as well as the surface properties of the studied system. The corresponding EIS (Nyquist) plot obtained was presented in **Fig. 5.** It is clear from the Nyquist plot that the addition of the inhibitor altered the impedance response. At all concentrations, the impedance spectrum exhibited similar pattern and is characterized by a single semicircle shaped capacitive loop in the high-frequency region and an inductive loop in the low-frequency area. The semicircle is reflective of a defensive layer formation of the inhibitor molecules on the CS surface, therefore illustrating the charge-transfer resistance associated with the corrosion phenomenon and the occurrence of the electrical double layer at the CS-acid solution interface [26]. Besides, the diameter of the semicircle becomes wider with increasing concentration of the inhibitor.
which signifies that better inhibitive performance could be achieved at higher concentration of the inhibitor.

The simulation and fitting of the Nyquist plot were conducted using a model circuit of the type in Fig.6. The values of impedance parameters such as the charge transfer resistance ($R_{ct}$), solution resistance ($R_s$), and the double layer capacitance ($C_{dl}$) obtained after fitting the EIS data to the equivalent circuit are listed in Table 4. It is worth mentioning that the depression in Nyquist semicircles is a feature for solid electrodes and often attributed to the frequency scattering, surface roughness and non-homogeneity of the solid electrode [26,27]. Therefore, the double layer capacitance ($C_{dl}$) was replaced by a constant phase element (CPE) in the equivalent circuit in order to obtain more accurate fit and justify the non-ideal behavior of the system. The impedance ($Z_{CPE}$) is defined by the following relation [20]:

$$Z_{CPE} = \frac{1}{Q(jw)^n} \quad (13)$$

where $Q$ represent the modulus of the CPE; $j$ is the imaginary root ($j^2 = -1$); $w$ denotes the angular frequency and $n$ represent the phase exponent which reflect the degree of irregularity. When $n = -1$, CPE denotes an inductor, for $n = 0$, a pure resistor, and for $n = 1$, a pure capacitor. The capacitance of double layer ($C_{dl}$) was evaluated using the following relation [24]:

$$C_{dl} = (QR_{ct}^{1-n})^{-1/n} \quad (14)$$

The thickness of the electrical double layer ($d$) is linked to the $C_{dl}$ according to the following equation [23]:

$$C_{dl} = \frac{\varepsilon \varepsilon_o A}{d} \quad (15)$$

where $\varepsilon$ denote the dielectric constant of the defensive layer; $\varepsilon_o$ is the vacuum permittivity; and $A$ represent the area of the electrode exposed to the corrosive medium. The inhibition efficiencies were calculated from $R_{ct}$ using the following equation:

$$\% \ IE_{EIS} = \frac{R_{ct} - R_{ct}^0}{R_{ct}^0} \times 100 \quad (16)$$

where $R_{ct}$and $R_{ct}^0$ represent the charge transfer resistance for CS in the presence and absence of the inhibitor, respectively.

The results displayed in Table 4 reveal that the charge transfer resistance ($R_{ct}$) values in the inhibitor-containing systems are remarkably higher than that of the blank system. This can be ascribed to the adsorption of inhibitor compounds on CS surface thereby obstructing it direct exposure to the corrosive medium. It was also observed that $R_{ct}$ values increase with increasing concentration of the inhibitor. This was linked to the increase in number of inhibitor molecules that bind to the CS surface. As a consequence, an increase in inhibition efficiency was observed and attain 86.85% at 600 mg L$^{-1}$. By contrast, the values of double layer capacitance ($C_{dl}$) at the CS-solution interface decreased with increase in inhibitor
concentration. This behavior was linked to lowering of the local dielectric constant occasioned by the gradual substitution of water molecules by inhibitor molecules at the electrode surface which in turn suggest that the inhibitor was adsorbed on both the anodic and cathodic reaction sites the on the surface [20]. Furthermore, the decrease in $C_{dl}$ values could also imply an increase in the thickness of a defensive layer at CS electrode surface which enhanced the corrosion resistance of the substrate [23].

![Fig. 5. Nyquist plots for CS in 0.5 M H$_2$SO$_4$ in the absence and presence of different concentrations of JPSE](image)

![Fig. 6. Equivalent electrical model circuit used to fit the EIS data](image)

<table>
<thead>
<tr>
<th>Conc. (mg L$^{-1}$)</th>
<th>$R_s$ (Ohm cm$^2$)</th>
<th>$C_{dl}$ (µF cm$^{-2}$)</th>
<th>$R_{ct}$ (Ohm cm$^2$)</th>
<th>% IE$_{EIS}$</th>
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</thead>
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<tr>
<td>Blank</td>
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<td>0.47</td>
<td>61.58</td>
<td>11.48</td>
<td>79.23</td>
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<td>0.74</td>
<td>55.01</td>
<td>18.10</td>
<td>86.85</td>
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</table>
3.5. Quantum chemical calculations

Geometry optimizations and quantum chemical computations were performed on the three main constituents of JPSE inhibitor using the B3LYP/DND model. The optimized molecular structures, HOMO and LUMO graphics of the examined compounds are displayed in Fig.7. The frontier molecular orbitals (FMOs) density distribution provide useful insight about the highest occupied molecular orbital (HOMO) of the inhibitor that may be responsible for forward donation of electrons pair to the unoccupied d-orbital of the iron and the lowest unoccupied molecular orbital (LUMO) of the inhibitor that may be liable to accept electrons pair from an electron-rich metal surface during back-bonding [23]. It can be seen from Fig. 7 that both the HOMO and LUMO densities of the three compounds are essentially distributed throughout the entire molecular structures. Such FMOs distribution in the compounds suggest that the O atoms of the hydroxyl and ether groups are able to donate their unshared electrons to empty d-orbital of Fe atoms, while the electron-deficient sites in the inhibitor molecules could also accept electrons from filled orbitals of metal atoms.

The numerical values of some electronic structure parameters of the molecules are reported in Table 5. The results show that fraxetin has the lowest value of $\Delta E$ (2.773), while gallic acid is characterized with the highest value of $\Delta E$(3.605) among the three compounds. It can be inferred from the $\Delta E$ results that fraxetin has lower stability than gallic acid and tomentin, which connotes higher reactivity or interaction with the CS surface. The molecular reactivity can also be correlated with chemical hardness ($\eta$), which describes the polarization capability of the molecule. Hard molecules are less reactive than soft molecules if electron transfer is necessary for the reaction [28]. The molecule with lower hardness tends to react readily and bind onto the metal surface, which results in better anticorrosion activity. In our case, the lowest value of $\eta$ was obtained for fraxetin(1.387) as compared to gallic acid (1.807) and tomentin (1.435). This affirms the strong propensity of fraxetin to bind to CS substate.

To evaluate the interfacial interactions between the investigated molecules and the CS surface, the fraction of transferred electrons ($\Delta N$) was computed using the work function of iron. It is evident from the data reported in Table 5 that fraxetin (0.429) exhibits the highest tendency to denote electrons to the CS surface, as compared to gallic acid (0.344) and tomentin (0.349). This finding highlights the affinity of fraxetin to form chemical bonds with the CS surface than gallic acid and tomentin.

The Fukui functions are employed to elucidate the local electron-donating and electron-accepting capability of the considered inhibitor molecules. The most probable site for nucleophilic attack is the atom/region in the molecule with the highest value of $f^+$ while the most favored site for electrophilic attack is the atom/region in the molecule with the highest value of $f^-$. The calculated values of the $f^+$ and $f^-$ for the non-hydrogen atoms are depicted in Table 6. For all the studied molecules, the favored sites for nucleophilic attack are the C atoms directly attached to electronegative groups. This is because these C atoms are electron-deficient and can easily accept charges when attacked by a nucleophilic reagent. Meanwhile, the preferred sites for electrophilic attack are essentially the carbonyl and hydroxyl O atoms.
of each inhibitor molecules. This is ascribed to high electron density of the O atoms, which make it possible for them to readily donate charge when attacked by an electrophilic reagent.

![Optimized geometry, HOMO, LUMO for Gallic acid, Fraxetin, Tomentin](image)

**Fig. 7.** The optimized structures and graphical surfaces of HOMO and LUMO of main JPSE constituents at B3LYP/DND level of theory.
Table 5. Quantum chemical parameters (eV) of the studied JPSE main constituents

<table>
<thead>
<tr>
<th>Constituents</th>
<th>$E_{HOMO}$</th>
<th>$E_{LUMO}$</th>
<th>$\Delta E$</th>
<th>$\eta$</th>
<th>$\chi$</th>
<th>$\Delta N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid</td>
<td>-5.388</td>
<td>-1.773</td>
<td>3.605</td>
<td>1.803</td>
<td>3.576</td>
<td>0.344</td>
</tr>
<tr>
<td>Fraxetin</td>
<td>-5.017</td>
<td>-2.244</td>
<td>2.773</td>
<td>1.387</td>
<td>3.631</td>
<td>0.429</td>
</tr>
<tr>
<td>Tomentin</td>
<td>-5.253</td>
<td>-2.383</td>
<td>2.870</td>
<td>1.435</td>
<td>3.818</td>
<td>0.349</td>
</tr>
</tbody>
</table>

Table 6. The Fukui functions of JPSE constituents (excluding H atoms) calculated at the B3LYP/DND level of theory

<table>
<thead>
<tr>
<th>Atom</th>
<th>$f_{\delta}^+$</th>
<th>$f_{\delta}^-$</th>
<th>Atom</th>
<th>$f_{\delta}^+$</th>
<th>$f_{\delta}^-$</th>
<th>Atom</th>
<th>$f_{\delta}^+$</th>
<th>$f_{\delta}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.073</td>
<td>0.026</td>
<td>C1</td>
<td>0.053</td>
<td>0.021</td>
<td>C1</td>
<td>0.109</td>
<td>0.038</td>
</tr>
<tr>
<td>C2</td>
<td>0.070</td>
<td>0.065</td>
<td>C2</td>
<td>0.062</td>
<td>0.049</td>
<td>C2</td>
<td>0.032</td>
<td>0.037</td>
</tr>
<tr>
<td>C3</td>
<td>0.066</td>
<td>0.010</td>
<td>C3</td>
<td>0.057</td>
<td>0.015</td>
<td>C3</td>
<td>0.057</td>
<td>0.034</td>
</tr>
<tr>
<td>C4</td>
<td>0.046</td>
<td>0.049</td>
<td>C4</td>
<td>0.023</td>
<td>0.021</td>
<td>C4</td>
<td>0.089</td>
<td>0.042</td>
</tr>
<tr>
<td>C5</td>
<td>0.091</td>
<td>0.030</td>
<td>C5</td>
<td>0.045</td>
<td>0.039</td>
<td>C5</td>
<td>0.090</td>
<td>0.076</td>
</tr>
<tr>
<td>C6</td>
<td>0.092</td>
<td>0.069</td>
<td>C6</td>
<td>0.026</td>
<td>0.042</td>
<td>C6</td>
<td>0.086</td>
<td>0.051</td>
</tr>
<tr>
<td>C7</td>
<td>0.089</td>
<td>0.037</td>
<td>C7</td>
<td>0.081</td>
<td>0.050</td>
<td>C7</td>
<td>0.050</td>
<td>0.049</td>
</tr>
<tr>
<td>C8</td>
<td>0.060</td>
<td>0.032</td>
<td>C8</td>
<td>0.083</td>
<td>0.032</td>
<td>O8</td>
<td>0.032</td>
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<tr>
<td>C9</td>
<td>0.028</td>
<td>0.023</td>
<td>C9</td>
<td>0.069</td>
<td>0.051</td>
<td>O9</td>
<td>0.051</td>
<td>0.085</td>
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<tr>
<td>O10</td>
<td>0.044</td>
<td>0.112</td>
<td>O10</td>
<td>0.043</td>
<td>0.099</td>
<td>O10</td>
<td>0.036</td>
<td>0.088</td>
</tr>
<tr>
<td>O11</td>
<td>0.031</td>
<td>0.089</td>
<td>O11</td>
<td>0.012</td>
<td>0.111</td>
<td>O11</td>
<td>0.056</td>
<td>0.112</td>
</tr>
<tr>
<td>O12</td>
<td>0.031</td>
<td>0.081</td>
<td>O12</td>
<td>0.030</td>
<td>0.094</td>
<td>O12</td>
<td>0.048</td>
<td>0.110</td>
</tr>
<tr>
<td>C13</td>
<td>0.029</td>
<td>0.041</td>
<td>C13</td>
<td>0.024</td>
<td>0.048</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>O14</td>
<td>0.019</td>
<td>0.084</td>
<td>O14</td>
<td>0.033</td>
<td>0.096</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C15</td>
<td>0.029</td>
<td>0.037</td>
<td>O15</td>
<td>0.050</td>
<td>0.097</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O16</td>
<td>0.044</td>
<td>0.110</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

3.6. Molecular dynamics simulation

MD simulations were carried out to theoretically examine the adsorption ability of chosen organic constituents of JPSE over the Fe (110) surface. Fig. 8 demonstrates the final equilibrated snapshots for each constituent derived from the final step of 500 ps MD simulations. It is apparent from these visualized snapshots that all the three inhibitor molecules were adsorbed on the Fe (110) surface. This theoretical finding suggests the tendency of the inhibitors to form a protective layer above the CS substrates. Additionally, it is evident from the side and top views of the displayed snapshots that the molecular backbone of surface-bound inhibitors presented a flat orientation with respect to the iron surface, which maximizes the surface coverage and anticorrosion characteristics of the studied inhibiting species. The
interfacial attachment of inhibiting species was also probed from a quantitative perspective and the resulting energetic features are recorded in Table 7. The energetic data presented in Table 7 reveal that the adsorption energies of all three molecules are negative, indicating the binding of the inhibiting agents to the CS surface. Moreover, the highest adsorption/binding energy values predicted for fraxetin reflects its strongest attachment to CS surface as compared with gallic acid and tomentin.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Total energy</th>
<th>Energy of molecule</th>
<th>Adsorption energy</th>
<th>Binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid</td>
<td>–104.03</td>
<td>–37.09</td>
<td>–66.94</td>
<td>66.94</td>
</tr>
<tr>
<td>Fraxetin</td>
<td>–139.97</td>
<td>–48.77</td>
<td>–91.20</td>
<td>91.20</td>
</tr>
<tr>
<td>Tomentin</td>
<td>–129.84</td>
<td>–41.55</td>
<td>–87.45</td>
<td>87.45</td>
</tr>
</tbody>
</table>

Fig. 8. The final snapshots of gallic acid, fraxetin, and tomentin inhibitors over Fe (110) surface.

Table 7. The energetic outputs (kcal mol⁻¹) obtained from molecular dynamics simulations of inhibitor molecules over the Fe (110) surface.
3.7. Surface characterization studies
SEM micrographs clearly depicting the abraded, corroded and inhibited surfaces are presented in Fig. 9. Before immersion, the abraded CS specimen presented a very smooth morphology (Fig. 9a). However, after immersion in the blank 0.5 M H₂SO₄ solution for 9 h, the CS presented a rough surface and apparent pits, which suggest a severe damage upon contact with aggressive solution (Fig. 9b). The aggressive agents can penetrate deep into the steel surface through these passages to form mordant corrosion products [26]. After immersion in the JPSE inhibitor test solution for 9 h, an even and uniformly coated surface of the CS substrate was noticed as depicted in Fig. 9(c-d). There were no traces of heaps of corrosion products on the surfaces, suggesting an efficient anticorrosive ability of the JPSE. Furthermore, the surface morphology of the inhibited specimens is comparable to that of the abraded specimen.

Fig. 9. SEM micrographs of the CS surfaces after (a) mechanical abrasion, (b) immersion in 0.5 M H₂SO₄ solution free of inhibitor, (c) immersion in 0.5 M H₂SO₄ solution containing 450 mg L⁻¹ JPSE, and (d) immersion in 0.5 M H₂SO₄ solution containing 600 mg L⁻¹ JPSE for 9 h at 30 °C.
3.8. Probable mechanism of corrosion inhibition

Generally, organic inhibitors retard the corrosion phenomenon by adsorbing on the corroding metal surface either physically or chemically. This involves the displacement of adsorbed water molecules on the metal surface by adsorbed inhibitor molecules [29]. Several parameters including the metal surface charge and the state of an inhibitor molecule in a corrosive medium have a significant influence on the adsorption mechanism [30]. According to the literature, the adsorption of an inhibiting species on a metallic surface can be explained based on three different forms of interactions [31,32]. These interactions include: electrostatic interactions between the charged inhibitor molecules and metal cations; coordination of metal atoms with the unshared pair of electrons of inhibitor molecules, and π electron participation of the organic molecule in the process of coordination. The inhibitive action of JPSE molecules can be linked to the unshared pair of electrons on the oxygen atoms which is readily available for sharing with empty d-orbital of iron atoms forming a coordinate covalent bond (chemisorption). Also, the π-electrons of the aromatic rings in the inhibitor molecules could form coordination bonds with the vacant d-orbital of iron atoms via donor–acceptor interactions.

To verify the formation of a complex between the inhibitor molecules and Fe ions, UV–visible experiments were performed. Fig.10 depicts the UV–visible spectra of JPSE in 0.5 M H₂SO₄ solution before and after the immersion of the CS specimen for 9 h at 30 °C.

![UV–visible spectra of JPSE in 0.5 M H₂SO₄ solution before and after immersion of the CS specimen for 9 h at 30 °C.](image)

**Fig. 10.** UV–visible spectra of JPSE in 0.5 M H₂SO₄ 15 solution before and after immersion of the CS specimen for 9 h at 30 °C.
It is apparent from the spectra that the JPSE solution presented only the characteristic $\pi \rightarrow \pi^*$ band at around 210 nm. However, in the UV–visible spectra of the JSPE + Fe ions solutions, a new band at about 350 nm was observed, which was ascribed to the complex formation between Fe and the inhibitor compounds [33]. This outcome verifies that the prevalent adsorption mechanism of JPSE on the CS surface in 0.5 M H$_2$SO$_4$ solution is chemisorption.

4. Conclusion

Herein, JPSE has been explored as a novel green corrosion inhibitor for CS in 0.5 M H$_2$SO$_4$ solution. The experimental results revealed that JPSE possess inhibiting effect toward the CS in the examined corrosive medium. From the weight-loss technique, 600 mg L$^{-1}$ JPSE inhibited the CS corrosion at 30 °C by 90.40%. The influence of temperature indicates that the inhibition efficiency of the tested inhibitor decreases with rising temperature. The potentiodynamic polarization studies verified that the JPSE exhibited a mixed-type inhibition effect with a cathodic dominance. EIS measurements revealed that in the presence of the inhibitor, the charge transfer resistance increases while the double layer capacitance decreases. The SEM results demonstrated that the JPSE is highly effective in mitigating the corrosion of CS in 0.5 M H$_2$SO$_4$ solution. The mechanism of chemisorption is proposed for the interaction of JPSE compounds with the CS surface, and the UV–visible results confirmed complex formation. The computational outcomes showed that the inhibitor molecules are adsorbed strongly on the CS surface, which justified the experimental results. The corrosion inhibition efficiency of JPSE from weight loss, PDP and EIS methods are in good agreement. Overall, JPSE is a promising candidate for the inhibition of CS corrosion in acidic medium.

References