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***Tithonia diversifolia* Extract as An Eco-friendly, High-temperature Corrosion Inhibitor for 304 Stainless Steel in Acidic Solution: Experimental and Quantum Chemical Studies**

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Abstract

In the present work, *Tithonia diversifolia* (Hemsl) A. Gray leaf extract (TDLE) was utilized as an eco-friendly and high-temperature corrosion inhibitor for 304 stainless steel (SS) in 1 M HCl. The performance of TDLE was studied electrochemically using potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The surface of the metal was characterized using scanning electron microscopy (SEM). The quantum chemical method was also studied to understand the inhibition process. Leaves were extracted with demineralized water at 90°C. The adsorption behavior of TDLE best matches Langmuir's adsorption isotherm. The isotherm assumed that the adsorbed species occupies only one surface site to form a monolayer of inhibitor on the metal surface with no interactions from other adsorbed species. The corrosion inhibition efficiency increases with solution temperature, reaching 98.48% at 65°C in the presence of 3.5 g/L TDLE. SEM images show significant improvement of the 304 SS surface with TDLE. A quantum chemical study indicates that methyl 3,5-dicaffeoyl quinate is the most active inhibitor in TDLE.

Keywords

Stainless steel, green inhibitor, acid inhibition, high-temperature corrosion, electrochemical calculation.

Introduction

Stainless steel (SS) type 304 has numerous applications in many industries due to its formability and corrosion resistance [1–4]. Industrial processes often produce undesirable mineral deposits (scale), rust, etc. on steel surfaces. Therefore, construction materials made from 304 SS require treatment after use [5–8]. This material should be immersed in an acid solution (known as a pickling process), such as hydrochloric acid (HCl), to remove scale [9, 10]. Unfortunately, the acid solution used in pickling not only dissolves scale, but also attacks the metal [9]. In addition, pickling is usually executed at 65–80°C [3, 9, 10]. High temperatures also accelerate corrosion; therefore, corrosion control is required.

Adding inhibitors to the pickling solution can protect the metal from the acid [9–11]. Organic inhibitors are commonly used as such inhibitors [12, 13]. The efficiency of an organic inhibitor is mainly attributed to π bonds and/or highly electronegative atoms or molecules, which can donate electrons to slow oxidation of the metal [14]. Recently, an organic inhibitor from natural products has been widely developed and applied. Almond gum, a mixture of rosemary and cinnamon cassia oil, *Pterocarpus santalinoides* leaf extract, *Thevetia peruviana* flower extract, *Nephelium lappaceum* extract, *Akebia trifoliata* koiaz peel extracts, and maple leaf extract can improve steel corrosion resistance in acid solution [9, 11, 15–19]. Unfortunately, these compounds do not inhibit 304 SS corrosion effectively at high temperatures. In the present work, we utilized an extract of *Tithonia diversifolia* (Hemsl) A. Gray leaves as an eco-friendly, high-temperature corrosion inhibitor for 304 SS in 1 M HCl. *Tithonia diversifolia* (Asteraceae) is a shrub known as kembang bulan or rondo semoyo in Indonesia [20]. This plant has only been used as a traditional medicine and livestock feed. Because *Tithonia* extract contains phenolic compounds, we decided to explore whether it could be used as an organic corrosion inhibitor [20, 21].

This study was conducted using scanning electron microscopy (SEM), and electrochemical and quantum chemicals methods. Effects of concentration and temperature on corrosion inhibition were also investigated. Furthermore, we identified the main compounds of TDLE using density functional theory (DFT) methods in GAMESS software to understand its corrosion inhibition better. This extract performs better than other bio-organic treatments mentioned above. At high temperatures, TDLE corrosion inhibition efficiency reached 98.5%, demonstrating its potential as an eco-friendly corrosion inhibitor at high temperatures.

Experimental Methods

Materials

Experiments were performed on a specimen of 304 stainless steel with composition (wt%): 0.08% C, 2.00% Mn, 0.045% P, 1.00% Si, 18.00% Cr, 8.00% Ni and the balance Fe. The 304 SS sheet was cut into rectangular samples with an exposed surface area of 1 cm². Furthermore, the surface area was abraded using emery paper of grades 500 and 1000 consecutively. Specimens were washed thoroughly with demineralized water and acetone and then dried prior to measurement.

Extracts of *Tithonia diversifolia* leaves were prepared as previously described [21]. Briefly, an aqueous extract was prepared from 67.75 g of powdered, dried leaves in demineralized water at 90°C. 2.5, 3.0, 3.5, and 4.0 g/L solutions were prepared by dissolving TDLE dry powder using 1 M HCl, prepared by diluting AR grade 37% HCl (Merck, Germany). The TDLE solvent was removed by evaporation and freeze-drying to yield a dry powder. All cleaning and diluting processes in this experiment used demineralized water.

Electrochemical Measurement

Electrochemical measurements were conducted using an Autolab PGSTAT128N equipped with Nova 1.11 software. A three-electrode cell system was used in all measurements unless otherwise described, with the 304 SS specimens as the working electrode (WE), the Ag/AgCl (KCl 3 M) as the reference electrode (RE), and platinum as the counter electrode (CE). Prior to measurements, all electrodes were immersed in the test solution at open-circuit potential (OCP) until steady state conditions were achieved.

Potentiodynamic Polarization Measurement

The applied potential for potentiodynamic polarization measurement was calculated from E_{corr} values obtained (at ± 700 mV) with a scan rate of 1 mV/s. Tafel plots were extrapolated at the intersection to obtain corrosion parameters (i_{corr} , E_{corr} , b_a , b_c , and C_R). Measurements at various inhibitor concentrations were carried out at room temperature (25°C). The temperature dependence of inhibition was investigated at 25-65°C.

Electrochemical Impedance Spectroscopy (EIS) Measurement

Impedance measurements were performed at OCP with a signal amplitude of 1 mA in the frequency range of 100 kHz to 0.1 Hz. The Nyquist plot was extrapolated to obtain the charge transfer resistance (R_{ct}), solution

resistance (R_s), and the constant phase element (CPE). All impedance measurements were conducted at room temperature.

Surface Analysis

Specimens of 304 SS were prepared as described in subsection "materials". Specimens were immersed in 1 M HCl in both the absence and presence of the inhibitor (3.5 g/L) for 9 days at room temperature. Afterward, specimens were washed with demineralized water and dried at ambient conditions. Surface morphologies of specimens with and without inhibitor were examined using an FEI Inspect S50 Scanning Electron Microscopy (SEM).

Computational Detail

Molecular sketches of extract components were drawn using Avogadro 1.2.0. All quantum calculations were performed with complete geometry optimization using the General Atomic and Molecular Electronic Structure System (GAMESS) software package. The correlation between inhibition efficiency of molecules and their electronic properties was investigated at the B3LYP level [22] with 6-31G* basis sets [23, 24]. The effect of solvent (water) also was elaborated in computational calculations. The result from the GAMESS calculation was processed with the Gabedit 2.4.8 package to determine quantum parameters. The following quantum parameters were calculated: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy band gap ($DE = E_{HOMO} - E_{LUMO}$), and the dipole moment (μ). Other parameters, such as ionization potential (I), electron affinity (A), chemical hardness (IE) and softness (σ), electronegativity (χ), and electron transferred (DN), were also calculated.

Results and Discussion

Potentiodynamic Polarization Measurement

The behavior of anodic and cathodic polarization with and without inhibitor in 1 M HCl is presented as a Tafel plot (Figure 1). Corresponding electrochemical parameters are shown in Table 1. Inhibition efficiency (IE%) was calculated from corrosion current density values in the absence (i_{corr}^0) and presence (i_{corr}) of inhibitor (Eq. 1).

$$IE\% = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100, (1)$$

According to Table 1, the corrosion rate decreases with increasing TDLE concentration (from 2.5 g/L to 3.5 g/L). However, higher inhibitor concentrations (more than 3.5 g/L) caused the corrosion rate to increase. This increasing corrosion rate occurs because the protective inhibitory layer on the surface of 304 SS re-dissolved into the bulk solution when the concentration exceeded its critical point [2]. The maximum inhibition efficiency reached 83.75% at 3.5 g/L TDLE.

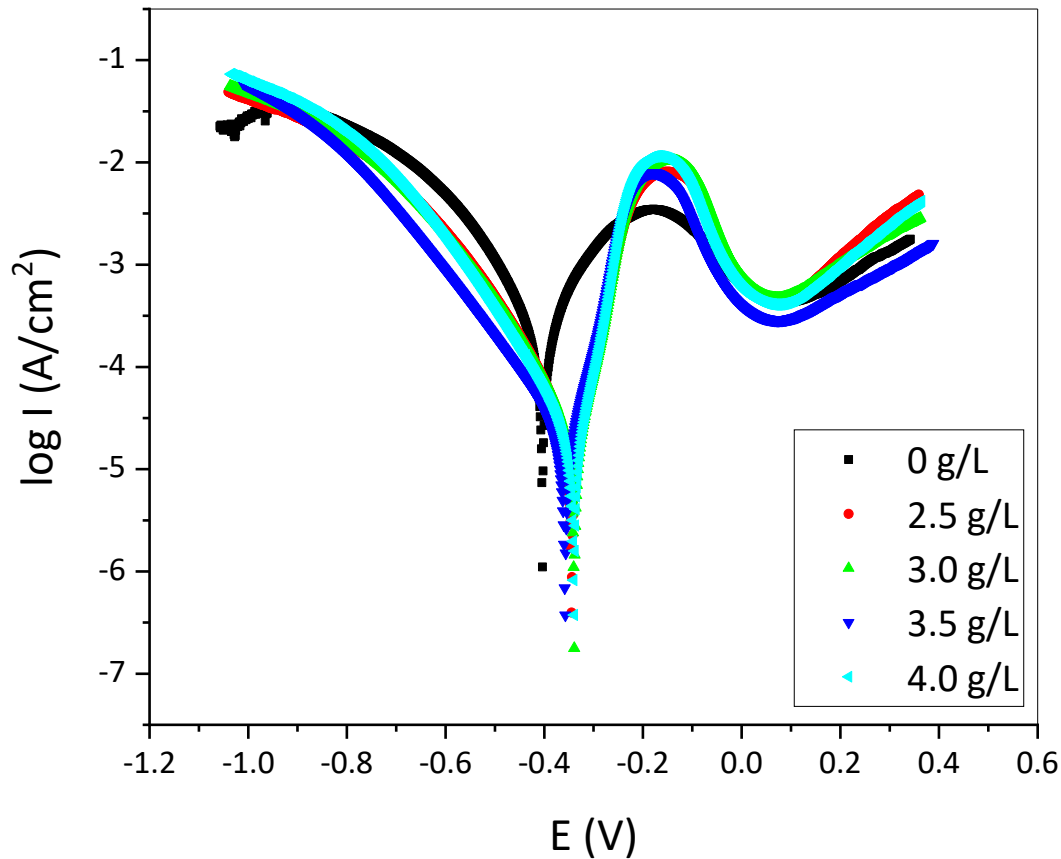


Figure 1. Polarization curves for 304 SS in 1 M HCl at various inhibitor concentrations.

The E_{bc} value remained almost unchanged upon inhibitor addition (Table 1). Adding an inhibitor to the solution did not affect hydrogen evolution [25]. The maximum E_{corr} of 304 SS shifted by 45.63 mV compared to the blank. Based on the literature, the inhibitor can be cathodic or anodic when the displacement in E_{corr} is more than 85 mV, and if the displacement of E_{corr} is less than 85 mV, the inhibitor acts as a well-known mixed type [2, 15]. Because the displacement of E_{corr} at TDLE is less than 85 mV, we suggest that it is a mixed type of corrosion inhibitor for 304 SS in 1 M HCl.

Table 1. Potentiodynamic polarization parameters for 304 SS in 1M HCl at different concentrations of the Tithonia inhibitor.

Concentration of TDLE (g/L)	b _a (mV/dec)	b _c (mV/dec)	E _{corr} (mV)	i _{corr} (μA)	j _{corr} (μA/cm ²)	C _R (mmpy)	IE (%)
0.0	81.869	68.721	-403.860	128.580	128.580	1.49410	-
2.5	982.970	687.150	-344.210	22.160	22.160	0.25750	82.76
3.0	102.140	634.550	-339.500	21.004	21.004	0.24407	83.66
3.5	131.570	723.460	-357.740	20.884	20.884	0.24267	83.75
4.0	136.150	701.960	-339.540	22.565	22.565	0.26220	82.45

Electrochemical Impedance Spectroscopy (EIS) Measurements

Nyquist plots of 304 SS with and without inhibitor in 1 M HCl are shown in Figure 2a. Semicircles in the Nyquist plots are attributed to various physical phenomena, such as roughness, active sites, and inhomogeneity of the solid surface [1, 2]. On the other hand, the impedance study provides information about the inhibition process in terms of the resistive and capacitive behavior of the metal or solution interface [10]. The diameter of the semicircles increased with increasing TDLE concentration (at 2.5-3.5 g/L), indicating a strengthening of the inhibitory layer (Figure 2a). A larger diameter gives a higher R_{ct} , which means a lower corrosion rate. Maximum inhibition occurred at 3.5 g/L of TDLE with $IE\% = 72.94$. The $IE\%$ value was calculated using Eq. (2).

$$IE\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100, (2)$$

where R_{ct} and R_{ct}^0 are the charge transfer resistance in the presence and absence of inhibitors.

Impedance parameters are summarized in Table 2. Figure 2b and 2c show Bode plots with and without inhibitors. Only one relaxation process can be observed, corresponding to one semicircular capacitive loop in the Nyquist plots. This behavior is attributed to an electrochemical system's time regular [26]. Figure 2d shows an equivalent circuit that is used to calculate the impedance parameter.

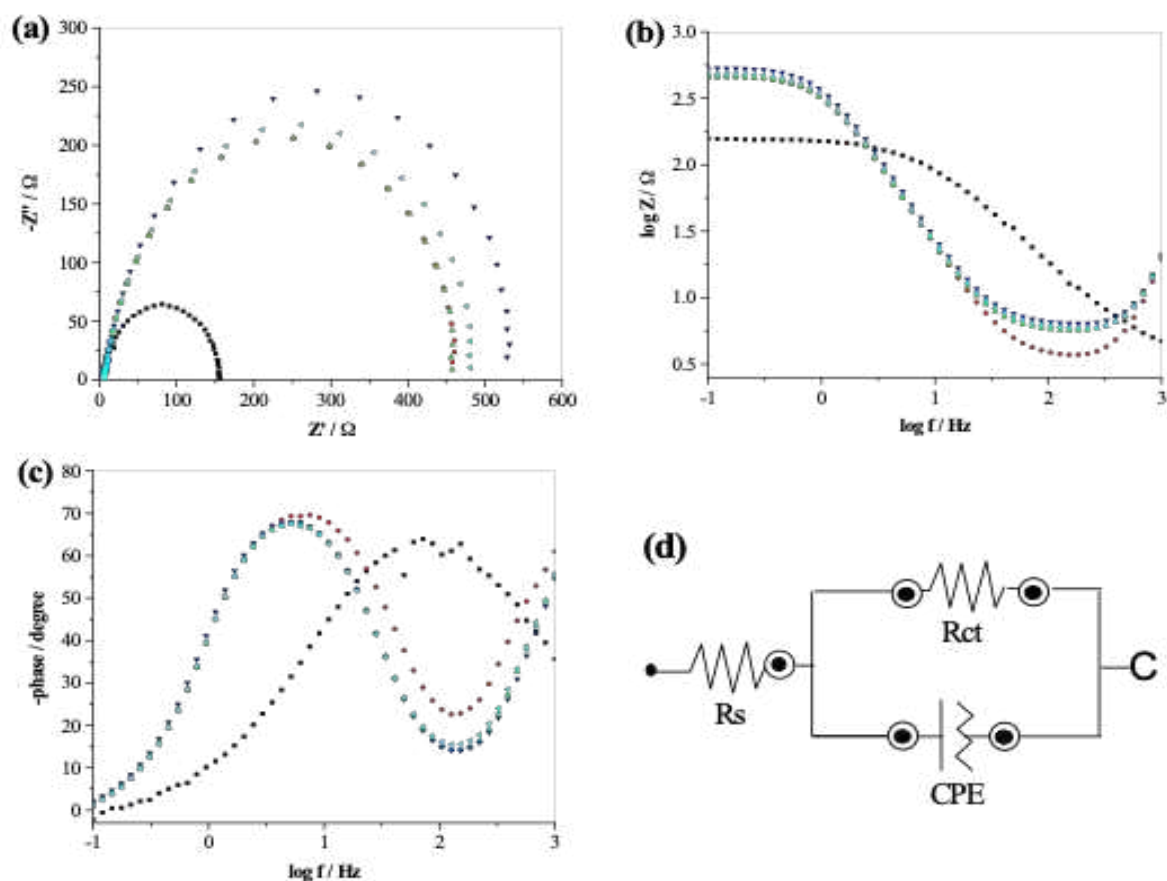


Figure 2. Nyquist plots (a), Bode plots: bode modulus (b) and bode phase (c) for 304 SS in 1 M HCl with various concentrations of inhibitor. Equivalent circuits used to fit EIS diagrams (c). 0 g/L (black), 2.5 g/L (red), 3.0 g/L (green), 3.5 g/L (blue), and 4.0 g/L (light blue) of inhibitor.

Table 2. Impedance parameters for 304 SS in 1 M HCl with various concentration of the Tithonia inhibitor.

Concentration of TDLE (g/L)	R_{ct} (Ω)	R_s (Ω)	CPE (μF)	χ^2	IE (%)
0.0	146.860	6.763	141.250	0.06867	-
2.5	461.540	8.439	108.290	0.09395	68.18
3.0	467.640	9.651	109.350	0.09735	68.56
3.5	542.890	12.525	100.340	0.14607	72.94
4.0	485.580	10.885	105.740	0.09674	69.75

Effect of temperature

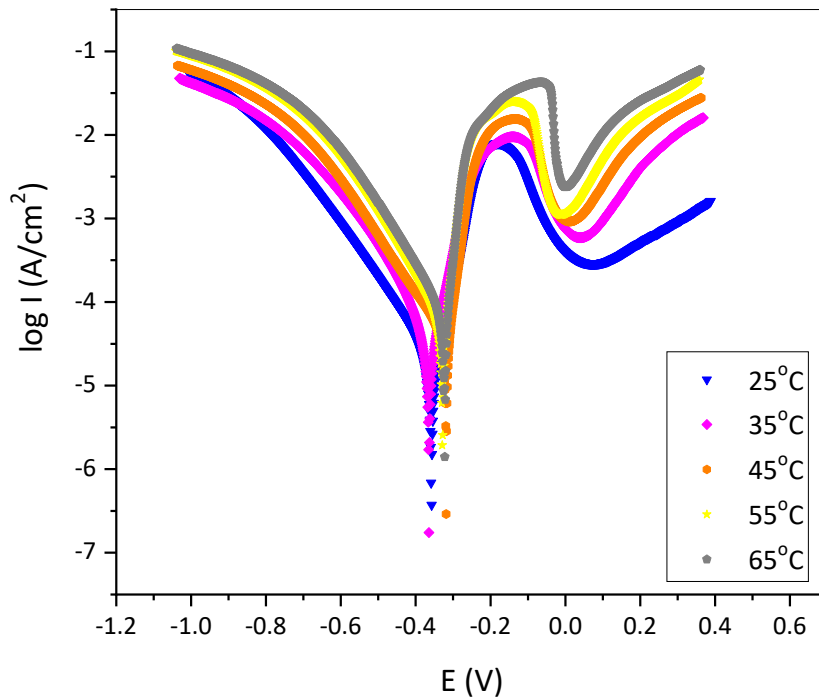


Figure 3. Polarization curves in the presence of 3.5 g/L inhibitor at various temperatures.

Figure 3 shows that the polarization curve of 304 SS in 1 M HCl with inhibitor continues to shift to the upper right, meaning that the current density increases with increasing temperature. The current density is directly proportional to the corrosion rate, so this result is in good agreement with theory. In general, the corrosion rate increases with temperature, because of a decrease in over-potential hydrogen evolution [15].

The corrosion rate increased with temperature in 1 M HCl without the inhibitor. In the presence of TDLE, the increasing corrosion rate is lower than without the inhibitor. Therefore, inhibition efficiency increases with increasing temperature (Table 3), indicating that a good protective layer formed on the 304 SS at high temperatures. Maximum inhibition efficiency was achieved at 65°C with $IE\% = 98.48$. This meant that the extract acts as an effective inhibitor at high-temperature.

Activation energy (E_a) is also important in order to demonstrate inhibitor performance. This value can be obtained from the Arrhenius equation (Eq. 3):

$$i_{corr} = Ae^{\left(\frac{-E_a}{RT}\right)}, (3)$$

Where i_{corr} is the corrosion current density, E_a is the corrosion reaction activation energy, and A is the Arrhenius pre-exponential factor. E_a values were calculated from linear plots obtained in Figure 4.

Activation parameters with and without inhibitors are summarized in Table 4, which shows that the E_a value with the inhibitor is lower than the E_a value without it. This result confirms that inhibition efficiency increases with temperature (Table 3). The inhibitor reduces the corrosion rate of 304 SS by chemisorption [27].

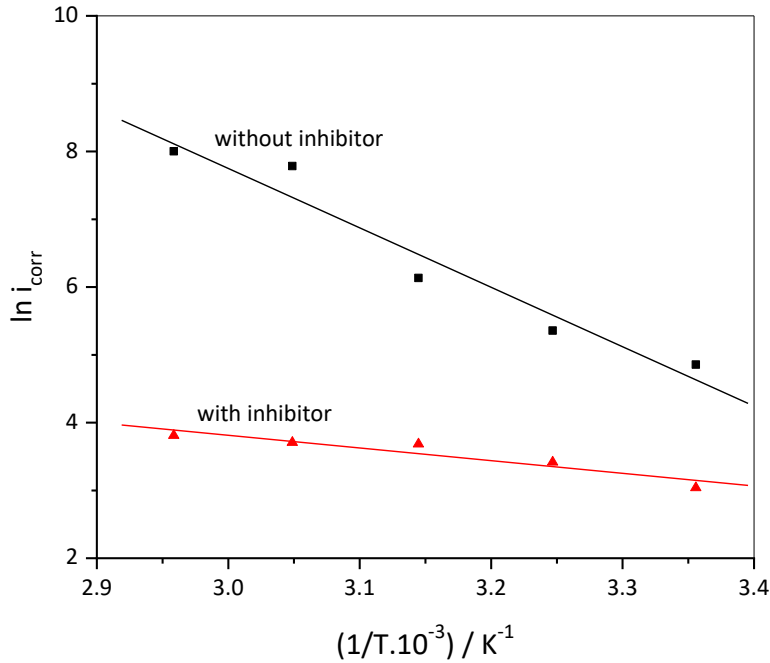


Figure 4. Arrhenius plots for $\ln i_{corr}$ vs. $1/T$ for 304 SS.

The Eyring transition state equation is an alternative formulation of the Arrhenius equation to determine the values of enthalpy (ΔH) and entropy (ΔS) [2, 15]. The values of ΔH and ΔS can be calculated by Eq. 4:

$$i_{corr} = \frac{RT}{N_A h} \exp \frac{\Delta S}{R} \exp - \frac{\Delta H}{RT}, (4)$$

Table 4 shows positive ΔH values for conditions with and without inhibitors. This positive value indicates the endothermic nature of the steel dissolution process [2, 28]. Values of ΔS with and without inhibitors are negative and positive, respectively. The absolute ΔS value in the presence of the inhibitor is larger than in its absence.

Large negative values of ΔS suggest that the activated complex in the rate-determining step represents an association rather than a dissociation step. It also implies that a decrease in disorder occurred from the reactants to the activated complex [29].

Table 3. Effect of temperature on corrosion inhibition of 304 SS by 3.5 g/L of Tithonia extract.

Temperature (°C)	Concentration of TDLE (g/L)	b_a (mV/dec)	b_c (mV/dec)	E_{corr} (mV)	i_{corr} (μ A)	j_{corr} (μ A/cm ²)	C_R (mmpy)	IE (%)
25	0.0	81.869	68.721	-403.860	128.580	128.580	1.4941	-
	3.5	131.570	72.346	-357.740	20.884	20.884	0.2426	83.75
35	0.0	118.970	76.201	-374.940	212.290	212.290	2.4668	-
	3.5	90.433	69.816	-364.480	30.473	30.473	0.3541	85.64
45	0.0	203.030	77.340	-359.240	460.790	460.790	5.3544	-
	3.5	160.350	39.472	-318.350	39.761	39.761	0.4620	91.37
55	0.0	172.970	75.675	-374.000	2403.000	2403.000	27.9230	-
	3.5	76.653	32.264	-328.370	40.737	40.737	0.4734	98.30
65	0.0	387.410	125.820	-357.320	2985.300	2985.300	34.6890	-
	3.5	82.328	23.644	-321.780	45.140	45.140	0.5245	98.48

Table 4. Activation parameter of 304 SS with and without inhibitor in 1 M HCl

System	E_a (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol)
without inhibitor	72.801	70.166	29.176
with inhibitor	15.531	12.896	-175.341

Adsorption isotherm study

The inhibition efficiency of TDLE depends on the adsorption degree of its constituents on the 304 SS surface.

To explain the adsorption of TDLE, several adsorption isotherms were calculated. Corresponding plots are shown in Figure 5, and Langmuir is shown in Figure 5a, Freundlich is demonstrated in Figure 5b, Temkin is shown in Figure 5c, and Frumkin is shown in Figure 5d. The closest fit, with $R^2 > 0.99$, was obtained from

Langmuir's isotherm (Eq. 5). It is assumed that the adsorbed species occupies only one surface site to form a monolayer of inhibitor on the metal surface with no interactions from other adsorbed species [26, 30].

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

where K_{ads} is the adsorption equilibrium constant, C is the concentration of TDLE, and θ (IE%/100) is the surface coverage. The value of K_{ads} was estimated from the Y intercept in the Langmuir plot (Figure 5a).

The K_{ads} value is then used to calculate the standard free energy of adsorption (ΔG) using Eq. 6:

$$\Delta G_{ads}^o = -RT \times \ln C_{H_2O} \times K_{ads}, \quad (6)$$

where C_{H_2O} (1000) is the water concentration in solution in g/L [31].

The ΔG_{ads}^o value of the inhibitor was -22.62 kJ/mol at 25°C. Generally, a negative value of ΔG_{ads}^o signifies the stability and spontaneity of the adsorption process [26]. A ΔG_{ads}^o value more than -20 kJ/mol suggests that chemisorption of TDLE components occurred on the 304 SS surface. This result is in a good agreement with those of the temperature effect experiment.

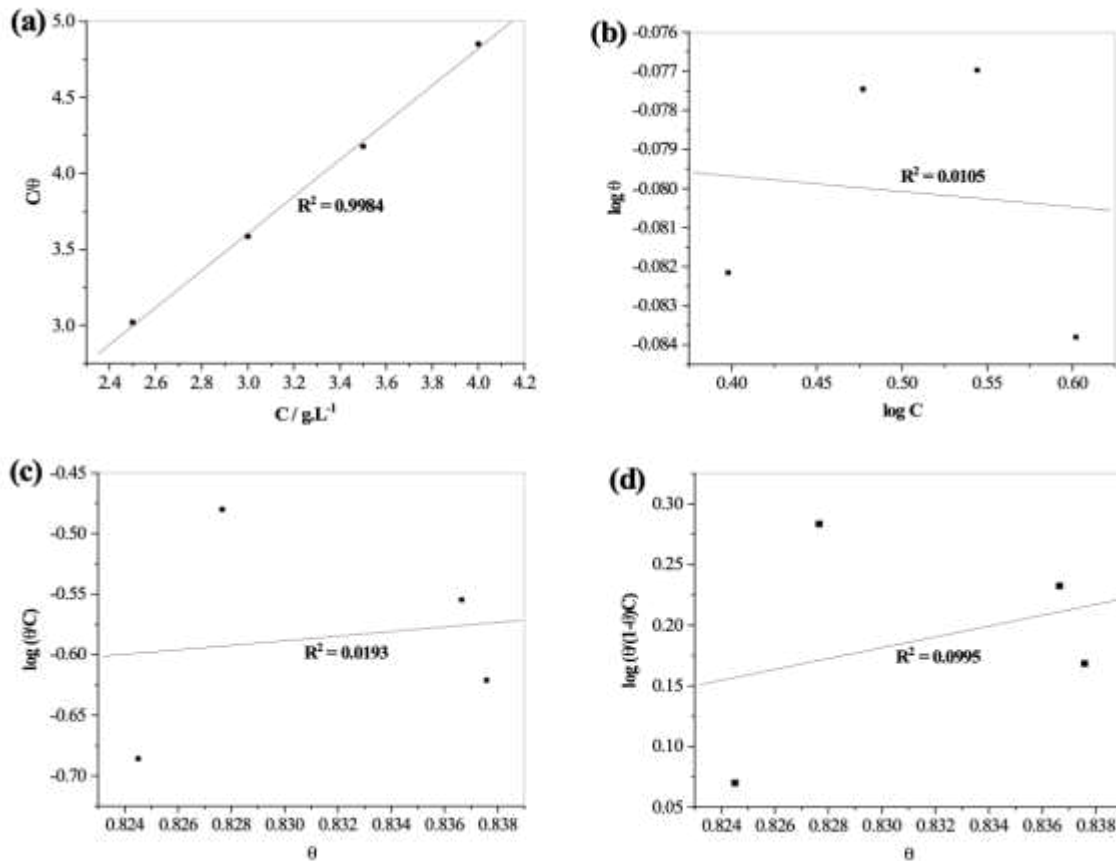


Figure 5. Langmuir (a), Freundlich (b), Temkin (c), and Frumkin isotherms (d) for adsorption of the inhibitor on the surface of 304 SS in 1 M HCl at 25°C.

Surface analysis

SEM analysis was performed to obtain information on the surface morphology of 304 SS. SEM images documented changes accompanying corrosion and protection on the 304 SS surface. Figure 6 shows SEM images of the 304 SS surface before and after corrosion. There is a significant improvement in the 304 SS surface, both with and without the corrosion inhibitor. Figure 6a shows the surface of 304 SS before the corrosion process, while Figure 6b shows the damage and a rough surface of 304 SS after it was corroded in 1 M HCl. The acid solution caused pits and black spots on the surface of 304 SS. Figure 6c revealed a protective layer formed by TDLE constituents, demonstrated by the smooth surface of 304 SS.

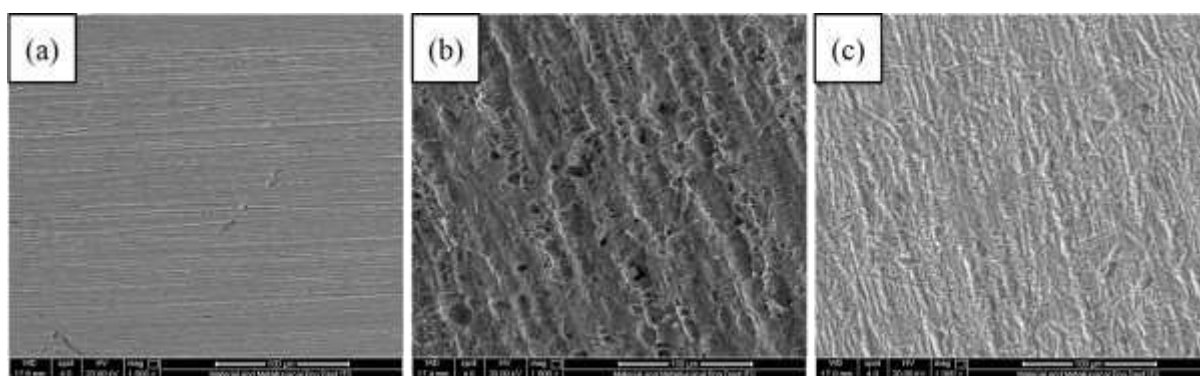


Figure 6. SEM images of the 304 SS surface before corrosion (a), after corrosion without inhibitor (b), and after corrosion with inhibitor (c) at 1000 times magnification.

Understanding the inhibition mechanism of TDLE by quantum chemical study

The effectiveness of a corrosion inhibitor is related to both its molecular spatial and electronic structures, in addition to its hydrophobicity and solubility [27]. *Tithonia diversifolia* contains secondary metabolites [20, 32]. Previous phytochemical investigations have reported the presence of sesquiterpenes [33], diterpenoids, quininic acids, and flavonoids [34]. Ziémons et al. identified tagitinin C as the primary compound of *T. diversifolia* extract using FTIR spectroscopy. This compound has a specific C=O stretching vibration at 1664.8 cm^{-1} [35]. Compared to our previous study, the FTIR analysis indicated a characteristic of the phenolic functional group [21] which includes O-H, C-O, and aromatic groups at wavenumbers 3398.80 cm^{-1} , 1124.54 cm^{-1} , and 1599.04 cm^{-1} respectively. Other studies report interesting, but different results due to the absence of the carbonyl group, judging from their FTIR spectra. Our results are very similar to those reported by Paula et al., suggesting that our TDLE contains an aromatic compound or ester without ketones [36]. These compounds in the extract made

it very difficult to assign effects to a particular constituent. Therefore, we investigated further to identify the main compounds using a computerized method in order to better understand corrosion inhibition of 304 SS by TDLE. The main compounds in our extract likely include methyl 3,5-dicaffeoyl quinate (1), 3,5-dicaffeoyl quinate (2), 5-O-(E)-caffeoylquinic acid (neochologenic acid) (3), 6''-O-b-D-apiofuranosyl-tricocarpin (4), protocatechuic acid (5), (-)-isolariciresinol-3a-O-b-o-glucopyranoside (6), arbutin (7), pinoresinol (8), and vanilloside (9) (Table 5).

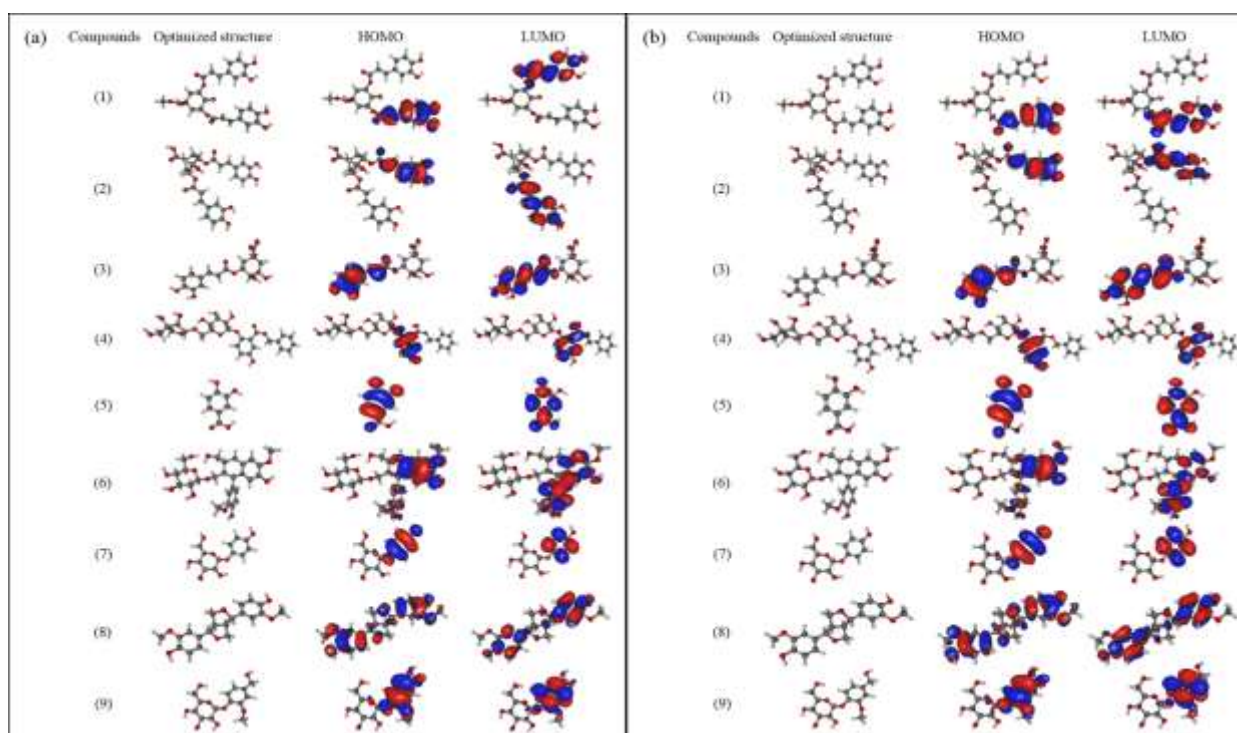
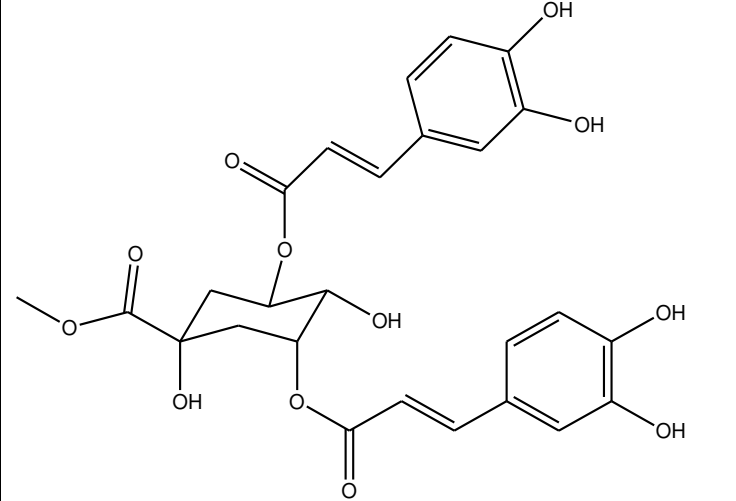
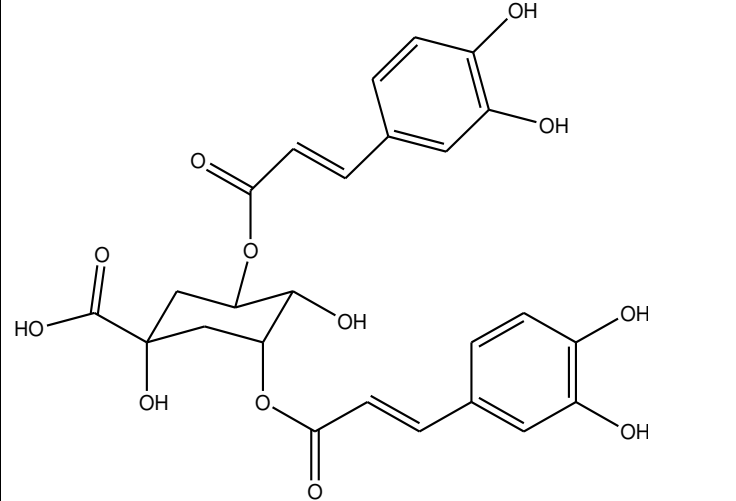
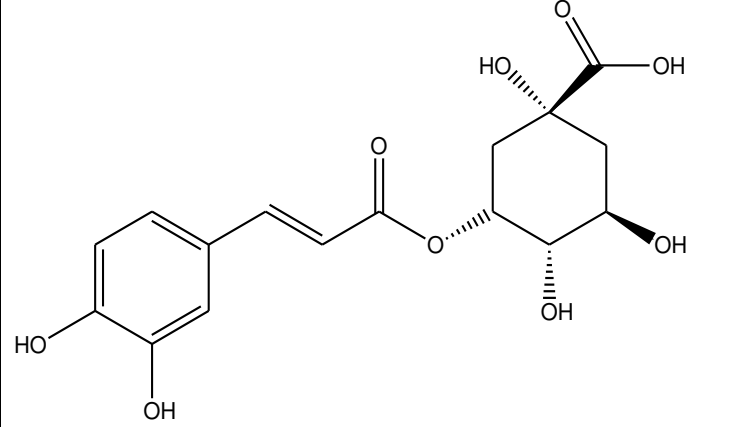
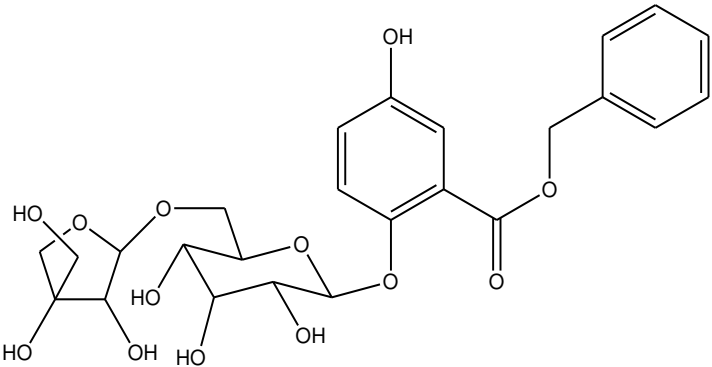
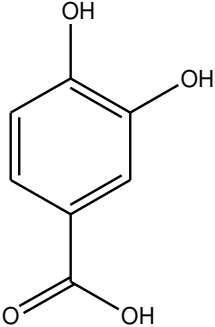
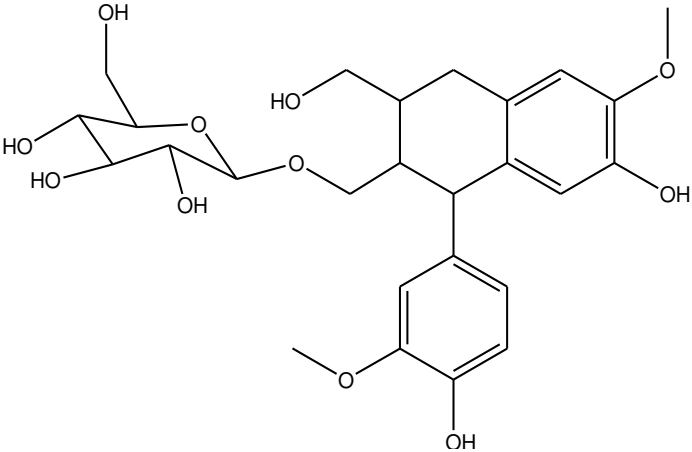


Figure 7. Optimized geometry, HOMO and LUMO, of compounds in TDLE in the absence (a) and presence (b) of the solvent.

Table 5. Chemical structure of the main component in TDLE.

No.	Compound	Name	Ref.
1.		methyl 3,5-dicaffeoyl quinate	[37, 38]
2.		3,5-dicaffeoyl quinate	[37, 38]
3.		5-O-(E)- caffeoylquinic acid or neochologenic acid	[36]

4.		6''-O-b-D- apiofuranosyl- tricocarpin	[37]
5.		protocatechuic acid	[37]
6.		(-)-isolariciresinol-3a- O-b-o- glucopyranoside	[37, 39]

7.		arbutin	[37]
8.		pinoresinol	[37]
9.		vanillobioside	[37]

Optimized geometries of the main compounds and their HOMO and LUMO distributions with and without solvents are shown in Figure 7a and 7b, respectively. Effects of quantum chemical parameters with and without solvent are summarized in Table 6. E_{HOMO} is the ability of molecules to donate electrons to the vacant d-orbital of Fe atoms on the surface. A higher E_{HOMO} value means that a molecule has greater capacity to donate its electrons to an acceptor (Fe), which has a larger number of vacant molecular orbitals, which determines an

inhibitor's capacity to prevent oxidation (corrosion) of the metal. On the other hand, E_{LUMO} is the tendency of electrons to accept the filled metal orbitals. The difference between E_{HOMO} and E_{LUMO} (ΔE) is an important parameter to determine molecule reactivity. A smaller ΔE value implies weaker molecular reactivity of an inhibitor molecule. Another implication of the energy difference is a corrosion inhibitor's tendency to take free electrons from the metal. Thus, a smaller ΔE signifies stronger adsorption of the inhibitor on the metal surface, increasing the inhibition efficiency [40, 41]. Table 6 shows a decreasing ΔE value in the order of $9 > 8 > 7 > 6 > 5 > 4 > 3 > 2 > 1$. The ΔE value (1) has the highest potential to adsorb Fe on the surface, forming a protective layer that protects the Fe from corrosive solutions. Another main quantum chemical parameter is the dipole moment (μ). The value of μ provides information to predict the direction of the corrosion inhibition process [27]. This value reflects the electron distribution and the polarity of the molecule. The higher the value of μ , the stronger the dipole-dipole interactions formed with the metal surface, resulting in better inhibition efficiency. However, there are no reports that discuss the correlation between μ and inhibition efficiency.

The E_{HOMO} and E_{LUMO} of the inhibitor correlate with their ionization potential (I) and the electron affinity (A), and these are measured using Koopman's theorem with the following equation [42, 43].

$$I = -E_{\text{HOMO}}, (7)$$

$$A = -E_{\text{LUMO}}, (8)$$

The electronegativity of an electron (χ) is obtained from the calculated value of I and A as follows:

$$\chi = \frac{(I + A)}{2}, (9)$$

The value of χ signifies the inhibitor's ability to attract electrons. A higher value of χ indicates a stronger attraction for electrons on the metal surface. The value for this inhibitor with high electronegativity suggests that the inhibitor strongly interacts with the metal surface, increasing inhibition efficiency.

The molecule's selectivity and reactivity affect the value of chemical hardness (η) and softness (σ). The value of η measures the resistance of an atom to a charge transfer, and σ describes the capacity of an atom or group of atoms to receive electrons. The value of η and σ is given by Saha et al. [40]:

$$\eta = \frac{(I - A)}{2}, (10)$$

$$\sigma = \frac{1}{\eta}, (11)$$

Soft molecules have smaller ΔE , which means they are more reactive, whereas hard molecules would have larger ΔE , which are less reactive [43]. According to Table 6, the ΔE of the inhibitor (1) has the highest value of σ and lowest value of η . These values show that its ΔE (1) is the softest, meaning that the Tithonia extract (1)

has better inhibition efficiency than other corrosion inhibitors due to a greater tendency to donate electrons to the metal. Values of χ and η were calculated in order to obtain the fraction of electrons transferred, ΔN . This parameter reveals the fraction of the electrons transferred from the inhibitor molecule to the metal surface, which can be calculated using the Pearson method (Eq. 12) [44].

$$\Delta N = \frac{\chi_{\text{metal}} - \chi_{\text{inh}}}{2(\eta_{\text{metal}} - \eta_{\text{inh}})}, \quad (12)$$

where χ_{metal} and η_{metal} are the electronegativity and chemical hardness of the metal, respectively, whereas χ_{inh} and η_{inh} are electronegativities and chemical hardness of the inhibitor molecule, respectively. In this study, we used the reported electronegativity and chemical hardness of iron (Fe), which are 4.06 eV and 3.81 eV [43, 45], respectively. If ΔN is less than 3.6, the inhibition efficiency increases with the electron-donating ability to the metal surface [43, 46]. ΔN values of all studied compounds are positive and less than 3.6 (Table 6), which indicates that the studied compounds can donate their electrons to the surface of Fe by forming coordinate bonds (chemisorption) [43]. Table 6 also shows that ΔN values of the studied compounds are slightly different. These ΔN values are relative values between molecules to show electron-donating ability. However, these values do not always represent the number of electrons leaving the donor and entering the acceptor molecule. Some reports state that the expression “electron-donating ability” is more appropriate than “number of transferred electrons” [40, 45].

Finally, based on its ΔE (1), methyl 3.5-dicaffeoyl quinate, has the largest potential to serve as an inhibitor in TDLE. The DFT calculation gave the same outcome as the experimental studies. Possible anticorrosive mechanisms are informed in Figure 8. All the main compounds in TDLE that interact with HCl solution are shown in Figure 8a. It shows that a thin layer was formed because of electron-donating, where methyl 3.5-dicaffeoyl quinate donated its electrons to the surface of 304 SS at ambient temperature. The strong layer was obtained at a high temperature (Figure 8b).

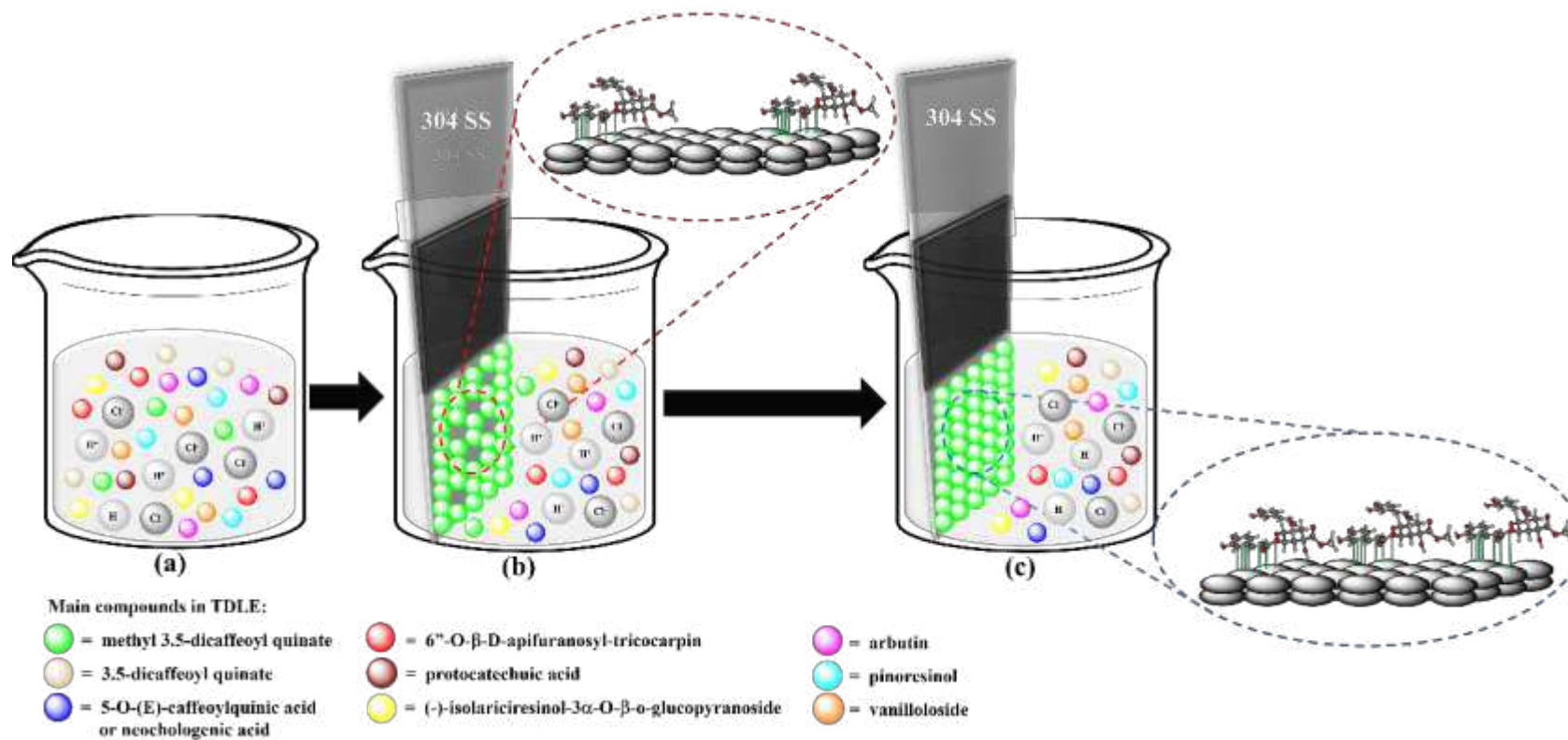


Figure 8. TDLE interactions in 1 M HCl solution (a) and possible mechanisms of the TDLE main compound in slowing corrosion of 304 SS in 1 M HCl at ambient temperature (b) and high temperature (c).

Table 6. The calculated quantum chemical parameters for the studied compounds in TDLE.

Method	Parameters	Compound								
		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
B3LYP/6-31G* without solvent	E _{HOMO} (eV)	-0.2035	-0.2087	-0.2107	-0.1957	-0.2236	-0.1920	-0.2051	-0.1160	-0.2096
	E _{LUMO} (eV)	-0.0539	-0.0575	-0.0550	-0.0320	-0.0405	0.0114	-0.0001	0.0967	0.0074
	ΔE (eV)	0.1496	0.1512	0.1557	0.1637	0.1831	0.2034	0.2050	0.2127	0.2170
	μ (D)	9.5355	7.6293	5.8844	13.1184	4.0230	4.5200	2.6011	0.2687	3.2091
	I	0.2035	0.2087	0.2107	0.1957	0.2236	0.1920	0.2051	0.1160	0.2096
	A	0.0539	0.0575	0.0550	0.0320	0.0405	-0.0114	0.0001	-0.0967	-0.0074
	η (eV)	0.0748	0.0756	0.0778	0.0818	0.0915	0.1017	0.1025	0.1063	0.1085
	σ (eV ⁻¹)	13.3689	13.2275	12.8452	12.2175	10.9229	9.8328	9.7560	9.4029	9.2166
	χ (eV)	0.1287	0.1331	0.1328	0.1138	0.1320	0.0903	0.1026	0.0096	0.1011
	ΔN (e)	0.5262	0.5258	0.5261	0.5292	0.5281	0.5352	0.5337	0.5468	0.5348
B3LYP/6-31G* with solvent	E _{HOMO} (eV)	-0.2086	-0.2102	-0.2112	-0.2081	-0.2202	-0.1975	-0.2097	-0.1204	-0.2189
	E _{LUMO} (eV)	-0.0647	-0.0629	-0.0619	-0.0504	-0.0408	0.0042	-0.0061	0.0905	-0.0014
	ΔE (eV)	0.1439	0.1473	0.1493	0.1577	0.1794	0.2017	0.2036	0.2109	0.2175
	μ (Debye)	12.6701	10.4699	9.3628	16.2963	4.6372	5.5325	3.0773	0.0112	4.2829
	I	0.2086	0.2102	0.2112	0.2081	0.2202	0.1975	0.2097	0.1204	0.2189
	A	0.0647	0.0629	0.0619	0.0504	0.0408	-0.0042	0.0061	-0.0905	0.0014

	η (eV)	0.07195	0.0736	0.0746	0.0788	0.0897	0.1008	0.1018	0.1054	0.1087
	σ (eV ⁻¹)	13.8985	13.5777	13.3958	12.6823	11.1483	9.9157	9.8231	9.4831	9.1954
	χ (eV)	0.1366	0.1366	0.1365	0.1292	0.1305	0.0966	0.1079	0.0149	0.1101
	ΔN (e)	0.5248	0.5250	0.5261	0.5267	0.5281	0.5342	0.5329	0.5459	0.5336

Conclusion

An extract of *Tithonia diversifolia* (Hemsl) A. Gray leaves acts as a good corrosion inhibitor for 304 SS in 1 M HCl solution at high temperatures. The highest inhibition efficiency reached was 98.48%, achieved by adding 3.5 g/L of extract at 65°C. Adsorption is spontaneous and matches the Langmuir adsorption isotherm. The free energy (-22.62 kJ/mol), enthalpy (12.896 kJ/mol), and entropy (-175.341 J/mol) indicated that for steel to adsorb the extract, a chemical adsorption process was involved. The study of the 304 SS surface using SEM shows formation of a protective layer by constituents of TDLE. Quantum chemical studies explained corrosion inhibition by TDLE. The results show that methyl 3,5-dicaffeoyl quinate has the smallest ΔE , the highest σ , and the lowest η compared to eight other compounds. This result further indicates that methyl 3,5-dicaffeoyl quinate has the highest potential to be adsorbed on the metal surface to form a protective layer. Based upon quantum chemical calculations, the adsorption mechanism is chemisorption, because the value of ΔN is positive and less than 3.6. This adsorption mechanism complies with adsorption isotherms.

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Competing Interests

There is no competing interest.

Data Availability Statement

All data generated or analyzed during this study are included in this published article.

Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Kartika A. Madurani and Soraya Firdausi. Project administration, resources, software, validation, and visualization were performed by Harmami, Ita Ulfin, Eviyanti Nazareth, Shaimah Rinda Sari, and Masato Tominaga. The first draft of the manuscript was written by Kartika A. Madurani and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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