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Eco-Friendly and Sustainable Inhibitors for Steel Corrosion in Acidic Media

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ABSTRACT

The inhibitory action of eco-friendly food waste extracts, namely Red Beta Vulgaris leaves (R.B.V.L) and Prunus cerasus seeds (P.C.S), against B7 grade steel corrosion in 1.0 M HCl was investigated utilizing chemical and electrochemical measurements. The study included the prediction of functional groups in both extracts using Fourier transform infrared spectroscopy (FTIR). Results from the potentiodynamic polarization technique indicated that both extracts act as mixed-type inhibitors, while electrochemical impedance spectroscopy revealed that corrosion process control is through charge transfer. Both R.B.V.L and P.C.S extracts exhibited a maximum inhibitory efficiency of 75%. The inhibition mode of both extracts was further studied using Langmuir and Flory-Huggins isotherms, as well as the Kinetic-thermodynamic model. Analysis of the change in free energy of adsorption, ΔG_{ads}, suggested physisorption (electrostatic) mechanism. Quantum chemical calculations were conducted to identify the main active ingredients.

1. Introduction

Corrosion is the most serious issue that scientists in the industry face [1–3]. Metal corrosion is influenced by a combination of factors, such as the type of media that causes corrosion [4–6]and the type of metal used to resist corrosion [7]. The petroleum industry is one of the most well-known industries. As a result, protecting petroleum pipelines and equipment is extremely important [8,9]. Several precautions have been taken to reduce corrosion phenomena [10]. One of them is the requirement to select a suitable type of corrosion inhibitor to reduce the rate of corrosion, which provides an economic benefit to the industry [11–13].

Corrosion and scale inhibitors are added throughout the operation to protect pipelines and heat exchangers in cooling water systems [14–16]. Acids are used in the pickling process to dissolve the scales, but they cause metal corrosion [17,18]. Many research papers are concerned with investigating corrosion inhibitors to decrease the corrosion rate caused by hydrochloric acid [19–26].

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Abd-El-Nabey *et al.,* [27] studied the inhibitory impact of extracts of the leaves of apricot, Morusnigra, and Alhagimaurorumon the steel corrosion in 0.5 M H_2SO_4 solution utilizing weight loss, thermometric, electrochemical impedance spectroscopy, and potentiodynamic polarization techniques. They found that the extracts are good corrosion inhibitors for the steel in 0.5 M H_2SO_4 solution. NA.Odewunmi *et al.,* examined the aqueous extracts of watermelon rind, watermelon seed, and watermelon peel extracts and found that the extracts are good inhibitors for steel corrosion in an acidic solution [28].

Due to environmental issues, many countries have initiated significant green chemistry innovations following the Paris climate change agreements [29,30]. Recognizing the economic benefits of reusing waste food rather than burning it, the importance of utilizing waste food for various purposes has become widely acknowledged [31]. In this context, several studies have been conducted to explore the potential of waste food and biomass as corrosion inhibitors [30,32,33]. Building upon this growing body of research, this study aims to investigate the inhibitory action of two eco-friendly food waste extracts, Red Beta Vulgaris Leaves (R.B.V.L) and Prunus Cerasus Seeds (P.C.S), against acidic corrosion of steel. Chemical and electrochemical techniques were employed to evaluate the effectiveness of these extracts as corrosion inhibitors for grade B7 steel in a 1.0 M HCl environment. Additionally, the influence of temperature on the corrosion inhibition process was examined.

2. Methodology

2.1 Solution Preparation

The 1.0 M hydrochloric acid (HCl) test solution was diluted with distilled water from 34% HCl (Scharlau Chemical Industries). Using the same procedure in our previous study, ethanolic extracts of R.B.V.L and P.C.S stock solutions were prepared. Ethanol is present in every test solution at a concentration of 10% [34].

2.2 Electrochemical Studies

The "Parstat 2263" equipment was used to carry out potentiodynamic polarization and electrochemical impedance spectroscopy "EIS" measurements. The EIS frequency range was 0.1–1×10^5 Hz, with a 10 mV applied potential signal amplitude around the open circuit potential. As counter and reference electrodes, platinum sheet and Ag/AgCl electrodes were employed. The composition of the used steel is (wt percent): 0.4 C, 0.9 Mn, 0.2 Mo, 1.0 Cr, 0.04 S, 0.035 P, 0.3 Si, and balance Fe. The exposed area (0.5 cm^2) was abraded with variable-grade emery papers. Just before inserting it into the test solution, it was carefully washed with double distilled water. To attain the open circuit potential, the electrode was left in the test solution for 15 minutes. Polarization curve measurements were taken at a 30 mV/min scanning rate starting from the cathodic to the anodic potential. Measurements were performed at 30.0 ± 0.1 ^oC using a WiseCircu water bath (Germany) in solutions open to the atmosphere. To study the temperature effect on steel corrosion and its inhibition, experiments were conducted at 40, 50, and 60 °C. Double-checked experiments assessed the measurements' repeatability and reliability, and the results were found to be consistent within 2% of error.

2.3 Weight Loss Measurements

Initially, the steel coupons were meticulously polished using sandpaper and cleaned. Subsequently, the specimens were washed with distilled water to remove any surface impurities. Following pretreatment, the specimens were weighed on an analytical balance to four decimal places, and the initial weights were recorded. They were then immersed in test solutions containing 1.0 M HCl solution for 3.0 hours at 303 K in the absence and presence of various inhibitor doses. At 45.0 minutes intervals, the specimens were carefully removed from the test solutions and underwent a meticulous cleaning procedure. This involved sequential washing with distilled water and cleaning with a sponge. After another rinse with distilled water, the specimens were subjected to a final wash with acetone to ensure thorough degreasing and dried in a desiccator. After completing the cleaning steps, the specimens were weighed again on an analytical balance, and the differences in weights at each interval were meticulously noted. This systematic approach to pretreatment and cleaning ensures the accuracy and reliability of the weight loss testing procedure, allowing for precise evaluation of corrosion behavior over time. The reported weight loss value is the mean of the three tests of three parallel samples, and the error was assessed by determining the standard deviation (σ). The results indicate that the standard deviation is less than 0.5.

2.4 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR analysis of both extracts was done by FTIR 8400S Shimadzu in the spectral region between 400 and 4000 cm^{-1}.

3. Results

3.1 FTIR Results

FTIR analysis was utilized in many research to point out the functional groups present in a given extract [35–37]. Figure 1 shows the FTIR spectra of R.B.V.L extract. R.B.V.L extract had a high amount of vitamin C, flavonoids, and polyphenols (betalains and betaine) [38]. The FTIR spectrum shows absorption bands for N-H group stretching (3406 cm^{-1}). Asymmetric CH_2 stretching (2926 cm^{-1}). The C=C stretch (1644 cm^{-1}). The overlapping stretching vibrations of C=C and C=O (1628 cm^{-1}). In-plane C-H bending (1323.36 cm^{-1}). P−O stretching (1101 cm^{-1}), C-O stretching in C-OH (1031.95 cm^{-1}), C−H bending at (776.73 cm^{-1}). The obtained bands are consistent with the chemical structures of betanin in the R.B.V.L [39], Figure 2.

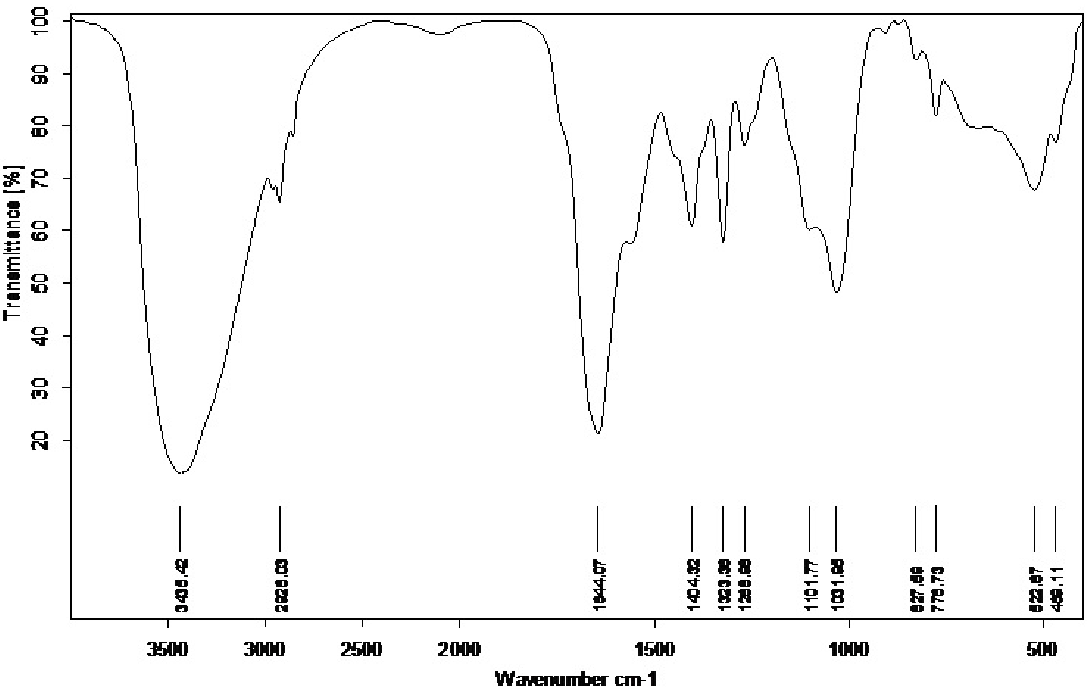


Fig. 1. FTIR spectra of R.B.V.L

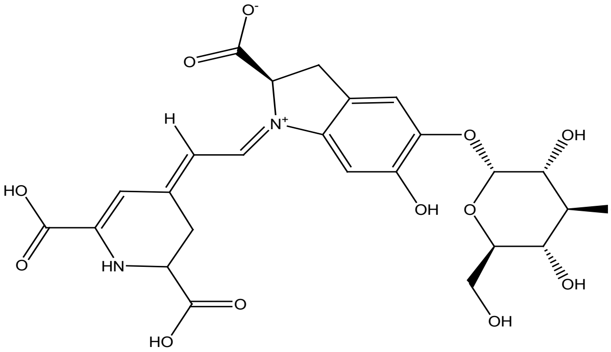


Fig. 2. Chemical structure of betanin

Istvan Bak *et al.,* [40] reported that P.C.S extract contains tocopherol-like components, tocotrienols, α-tocopherol, oleic acids, and 32–36% of vegetable oils. The solid part of P.C.S extract has many components, including 1% of catechins, 1% of stilbenes, 1% of trans-resveratrol, 1–2% of pro-and anthocyanidins, 1–3% of vegetable acids, 1–4% of flavonoids, 1–3% of polyphenols, and2–4% of cyanides. PCS extract is a flavonoid and a flavin-rich extract.

Figure 3 shows the FTIR spectra of the P.C.S extract. The spectrum shows absorption band for alcoholic O–H stretch (3439 cm^{-1}), phenolic O–H stretch vibration (3389.09 cm^{-1}), alkene C-H stretch (3009.01 cm^{-1}, and 2855.66 cm^{-1}), CH_2 stretching (2926.41 cm^{-1}), the carboxylic group appears at (1745.75 cm^{-1}, 1653.21cm^{-1}), C=N stretch (1546.28 cm^{-1}), alkene C-H bend (1459.30cm^{-1}), in-plane bending of phenolic OH (1375.31 cm^{-1}). In-plane aromatic C-H bending (1240.94 cm^{-1}), C-N stretch (1157.69 cm^{-1}). The vibration of C-O in the C-O-C group (1080.58 cm^{-}), C-H bending (717.40 cm^{-1}), and out-of-plane bending of aromatic C-H (560.70 cm^{-1}).The obtained bands were found to match the chemical structure of Flavin, Figure 4.

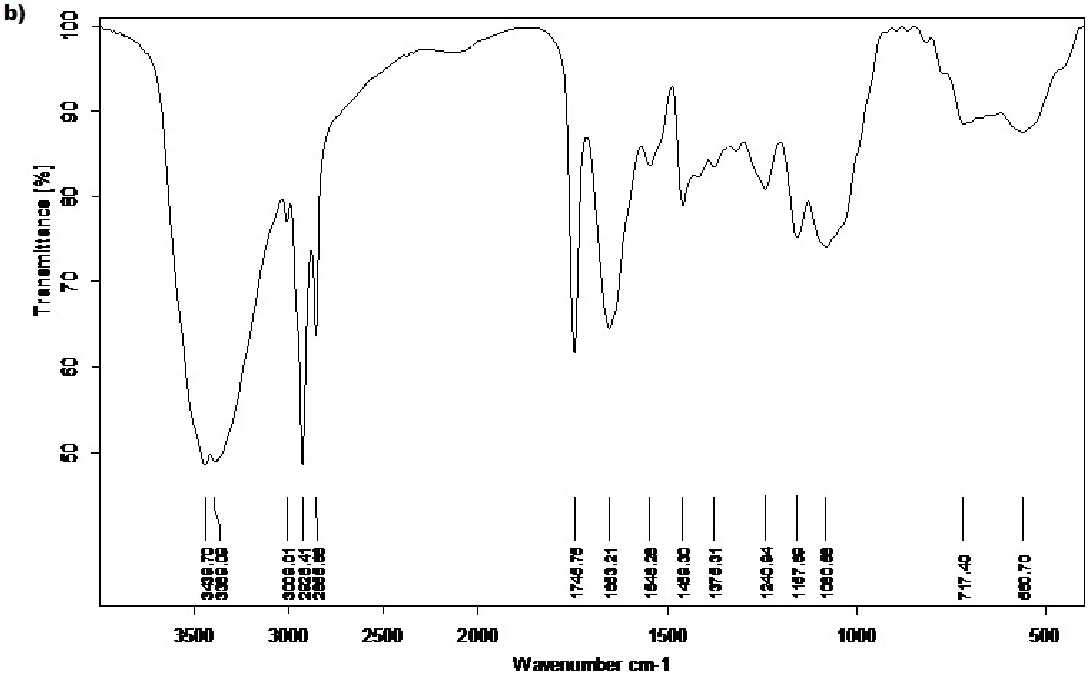


Fig. 3. FTIR spectra of P.C.S.

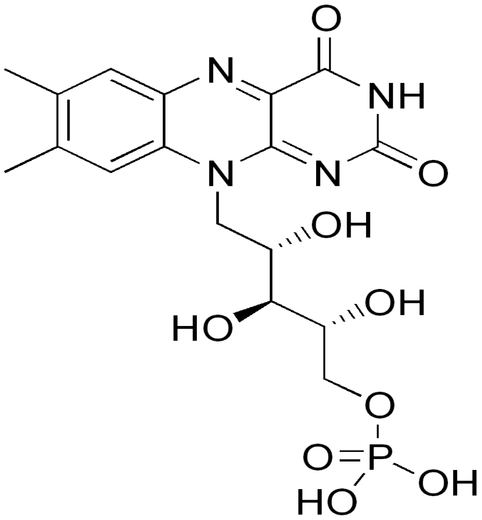


Fig. 4. Chemical structure for Flavin

3.2 Potentiodynamic Polarization Measurements

Figure 5 shows that increasing P.C.S extract concentration suppresses both the anodic and cathodic reactions indicating that P.C.S extract is a mixed-type inhibitor. A similar observation was recorded for R.B.V.L extracts (not shown). Table 1 lists the electrochemical polarization parameters.

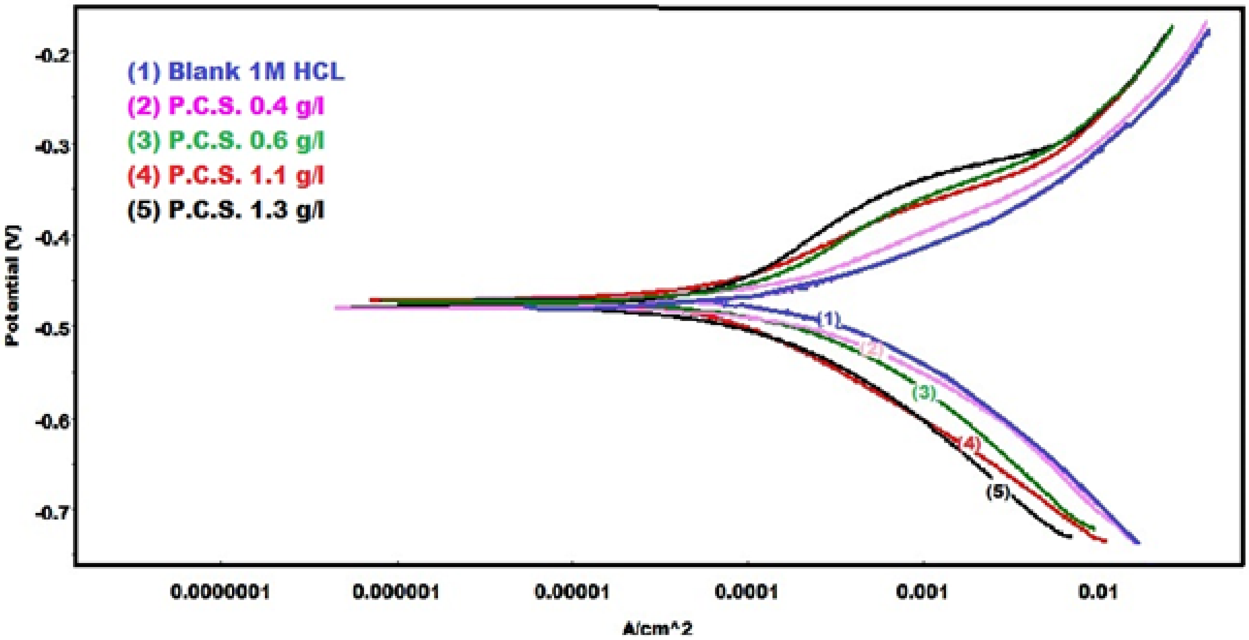


Fig. 5. Polarization plots for steel in 1.0 M HCl in the absence and presence of various concentrations of P.C.S extract at 30 °C

Table 1
The polarization parameters for the steel corrosion in 1.0 M HCl containing various concentrations of R.B.V.L and P.C.S extracts, respectively, at 30 °C.

	[Extract], g/L	$-E_{corr}$ (mV)	i_{corr} ($\mu A\ cm^{-2}$)	β_a mV/decade	$-\beta_c$ mV/decade	% η
	0.00	449	607	73	159	
R.B.V.L	0.065	447	334	71	173	44.9
	0.095	447	278	80	152	54.2
	0.150	447	225	91	153	62.9
	0.250	447	166	71	140	72.7
P.C.S	0.400	454	409	80	125	32.6
	0.600	444	355	117	158	41.5
	1.100	452	210	91	142	65.4
	1.300	459	142	112	128	76.6

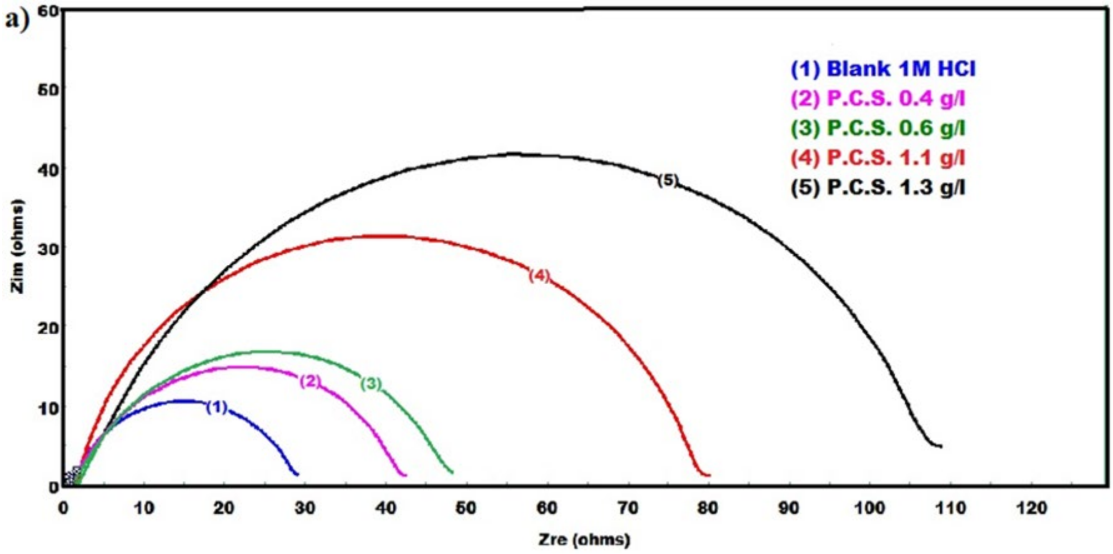
Using Eq. (1), the percentage inhibition efficiency (%) was determined [41]:

$$\%\ \eta = [(i_{corr}^{o} - i_{corr}) / i_{corr}^{o}]x100 \quad (1)$$

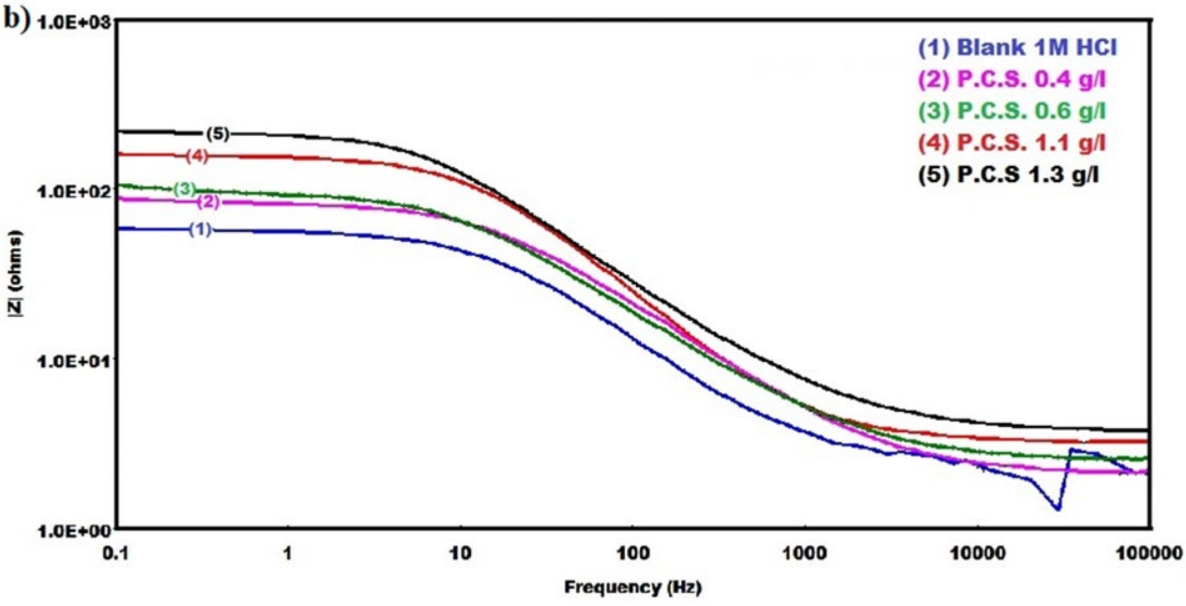
where i_{corr}^{o} and i_{corr} are the corrosion current densities in the absence and presence of extract. The i_{corr} values decrease, and the %η increase with an increase in the concentration of both extracts. This indicates that both extracts are good corrosion inhibitors for B7 grade steel in 1.0 M HCl, and the R.B.V.L extract is more effective at low concentrations. The slight variation in the corrosion potential (E_{corr}) suggests that the extracts could act as pickling inhibitors. The little difference in the anodic and cathodic Tafel slope values (β_a and β_c) confirms that increasing the concentration of the extracts does not affect their inhibition mechanism. The inhibition efficiency of R.B.V.L and P.C.S extracts surpasses previously reported values [42,43] while falling below previously documented values [44,45].

3.4 EIS Measurements

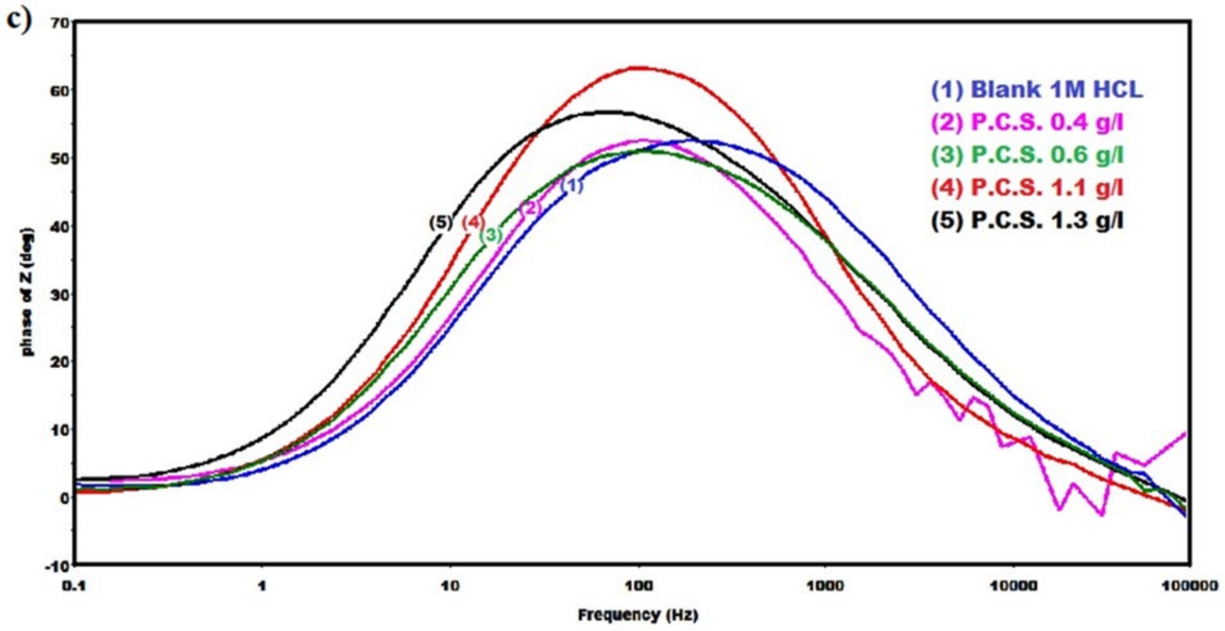
Figure 6 depicts Nyquist and Bode plots of steel in 1.0 M HCl in the presence and absence of different P.C.S extract concentrations. The Nyquist plots are characterized by a single depressed capacitive semicircle, illustrating that the charge transfer is the factor controlling the corrosion process [46]. Similarities of the Nyquist plots in the absence or presence of the extracts indicate that the corrosion process occurs via the same mechanism [47]. A similar observation was recorded for R.B.V.L extracts (not shown).



(a)



(b)



(c)

Fig. 6. a) Nyquist and b),c) Bode plots for steel in 1.0 M HCl in the absence and presence of different concentrations of P.C.S extracts at 30 ° C

The Zsimpwin program was utilized to fit the experimental data to the equivalent circuit model displayed in Figure 7.

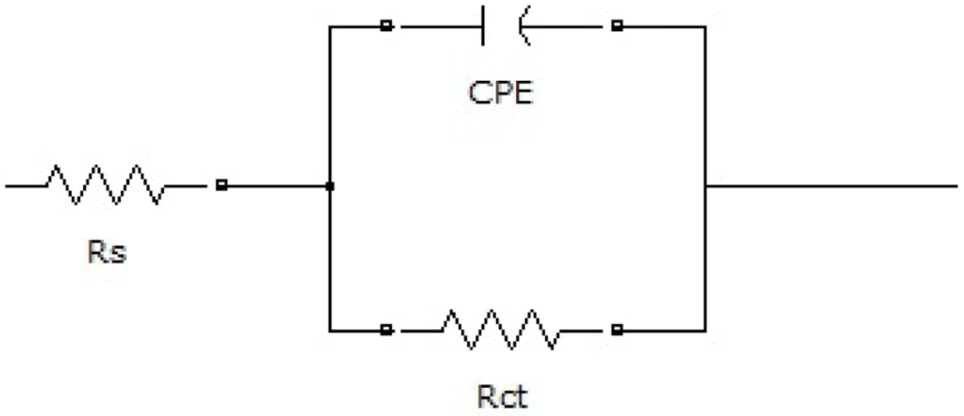


Fig. 7. The equivalent circuit model

In a non-homogenous system, the capacitances are donated as a constant phase element (CPE) that is donated by two values, Q and n. The capacitance of a non-ideal double-layer Q, in $\mu s^n/\Omega\ cm^2$, is numerically equal to the admittance (Y_o). The ideal capacitance of the double-layer (C_{dl}) was obtained using Eq. (2) [48].

$$C_{dl}= (y_0 \times R_{ct})^{1/n}/R_{ct} \tag{2}$$

Furthermore, the Bode diagrams of the P.C.S extracts at 30 ° C exhibit one distinct time constant which is attributed to the presence of double electric layer capacitance and charge transfer resistance. The inhibited steel demonstrates higher impedance at low frequencies on the Bode plots compared to bare steel. This confirms that the steel substrate is being effectively shielded by the P.C.S extracts [49,50].

Table 2 shows the obtained EIS parameters. The % η was calculated using Eq. (3) [51]:

$$\% \eta = [(R_{ct} - R^{o}_{ct}) / R_{ct}] \times 100 \quad (3)$$

where R_{ct} and R^{o}_{ct} are the charge transfer resistance in the presence and absence of extract.

The data indicate that, as the concentrations of both extracts increase, the R_{ct} and % η increase. The adsorption of the R.B.V.L. and P.C.S chemical constituents at the steel surface leads to a decrease in the C_{dl} values.

Table 2
The EIS parameters for the steel corrosion in 1.0 M HCl containing various concentrations of R.B.V.L and P.C.S extracts at 30 °C

	[Extract], g/L	R_s, (Ω cm^2)	R_{ct}, (Ω cm^2)	Q, Yo µs^n/Ωcm^2	n	C_{dl}, (µF/Cm^2)	% η	σ^2 (chi-squared)
	0.00	1.23	28	69.7	0.81	411	-	1.3×10^{-3}
R.B.V.L	0.065	1.70	47	56.1	0.80	402	41.0	1.3×10^{-3}
	0.095	1.60	59	52.5	0.80	392	52.5	3.2×10^{-3}
	0.150	1.59	74	49.0	0.81	335	62.1	1.9×10^{-3}
	0.250	1.13	96	35.6	0.79	309	71.0	2.6×10^{-3}
P.C.S	0.40	1.01	41	51.7	0.79	396	31.7	1.1×10^{-4}
	0.60	1.27	49	40.7	0.78	347	42.9	3.7×10^{-3}
	1.10	1.16	67	35.8	0.79	283	58.2	6.8×10^{-3}
	1.30	1.51	112	30.1	0.80	229	75.0	7.4×10^{-3}

3.5 Weight Loss Measurements

Table 3 displays the corrosion rate values (g/cm^2.hr) and %η for different R.B.V.L and P.C.S extract concentrations obtained from the weight loss method. The % η was determined using Eq. (4):

$$\% \eta = [(w_o - w)/w_o] \times 100 \quad (4)$$

where w and w_o are the corrosion rates in the presence and absence of the inhibitor, respectively. Table 3 shows that an increase in the extract concentration results in a decrease in corrosion rate and an increase in % η. At the concentration 0.25 g/L of R.B.V.L and 1.3 g/L of P.C.S, the inhibition efficiency attains about 75% for R.B.V.L, and 74.8% for P.C.S, indicating that both extracts are good inhibitors.

Table 3
Weight loss measurements in the absence and presence of different concentrations of extracts at 30°C

R.B.V.L				P.C.S			
Conc., g/L	Rate, g/cm^3.hr	%η	σ	Conc., g/L	Rate, g/cm^3.hr	%η	σ
0.00	0.01127	-	0.1	0.00	0.01127	-	0.1
0.065	0.00622	44.67	0.15	0.40	0.00775	31.25	0.2
0.095	0.00487	56.77	0.1	0.60	0.00647	42.55	0.15
0.150	0.00385	65.8	0.3	1.10	0.00376	66.61	0.3
0.250	0.00281	75.0	0.25	1.30	0.00284	74.8	0.1

Figure 8 depicts that the adsorption isotherm has a steeply increasing initial part showing the creation of a monolayer coating on the steel surface. The figure also illustrates a good agreement between the three methodologies' outcomes.

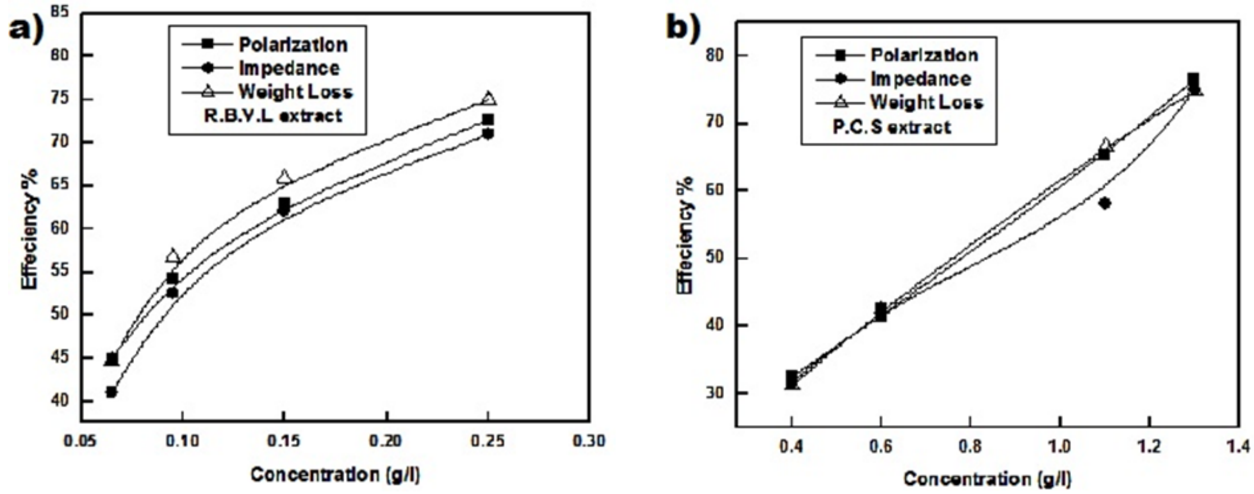


Fig. 8. Comparison of the inhibition efficiency of polarization, impedance, and weight loss techniques for a) R.B.V.L and b) P.C.S extracts

3.6 Adsorption Isotherm

Figures 9 to Figure 11 show the theoretical fitting of Langmuir and Flory-Huggins adsorption isotherms, as well as the Kinetic-thermodynamic model to experimental data obtained from polarization curves measurements [52–54]. The degrees of surface coverage values were estimated utilizing Eq. (5):

$$\theta = \%\eta/100 \quad (5)$$

The fitting parameters are given in Table 4. Figure 9 explains that Langmuir adsorption isotherm fits the experimental data in the R.B.V.L extract only as it gives a straight line passing through the origin, demonstrating ideal adsorption behavior.

Table 4
Adsorption parameters resulted from fitting the experimental data to the Langmuir and Flory-Huggins adsorption isotherms as well as the Kinetic-thermodynamics model for R.B.V.L and P.C.S extracts. The average absolute deviation (ADD) is used to evaluate the fitting results.

Model	Kinetic-thermodynamics model				Flory-Huggins isotherm			Langmuir isotherm		
Parameter	1/y	K	R^2	AAD	X	K	R^2	K	R^2	AAD
R.B.V.L	1.04	13.03	0.99	0.008	1.07	12.75	0.99	11.539	0.99	0.010
P.C.S	0.63	1.457	0.99	0.009	0.3	2.86	0.99	--	--	--

The application of the Kinetic-thermodynamic model is shown in Figure 10. The number of active sites that a single inhibitor molecule can occupy (1/y) for R.B.V.L and P.C.S extracts is 1.048 and 0.633, respectively. The bond strength between adsorbate and adsorbent is denoted by the value of the binding constant K. A High numerical value of K for R.B.V.L extract implies better and stronger interaction. In contrast, the lower value of K for P.C.S extract means that there is a weaker interaction between the extract's active ingredient and the metal surface. Figure 11 depicts the theoretical fitting of Flory-Huggins adsorption isotherm to the experimental data. This isotherm fitted for both extracts with x, counts the number of adsorbed water molecules that an inhibitor molecule replaces, value for R.B.V.L and P.C.S extracts equals 1.07 and 0.3 respectively.

The binding constant obtained from the Kinetic-thermodynamics model is related to the standard free energy of adsorption, ΔG_{ads}, with Eq. (6):

$$K = 1/55.5e^{(-\Delta G ads/RT)} \tag{6}$$

where R is the molar gas constant, T is the absolute temperature in Kelvin, and 55.5 is the concentration of water in solution expressed in molar [53]. The calculated ΔG_{ads} are -16.8 and -12.4 kJ mol^{-1} for R.B.V.L and P.C.S extracts, respectively. The negative values of ΔG_{ads} refer to the spontaneity with which both extracts adsorb. The physisorption mechanism is revealed by the acquired ΔG_{ads} values [55].

The used adsorption isotherm provides different insights into the adsorption mechanisms. The Langmuir adsorption isotherm demonstrated ideal adsorption behavior for the R.B.V.L extract, as evidenced by the straight line passing through the origin in Figure 9. The application of the Flory-Huggins adsorption isotherm yielded significant insights into the adsorption behavior of both R.B.V.L and P.C.S extracts. The obtained x values, representing the number of adsorbed water molecules replaced by an inhibitor molecule, were 1.07 for R.B.V.L and 0.3 for P.C.S extracts. This observation indicates that each inhibitor molecule from the R.B.V.L extract can displace approximately 1.07 water molecules upon adsorption onto the metal surface. In contrast, for the P.C.S extract, the corresponding value suggests that each inhibitor molecule replaces approximately 0.3 water molecules during the adsorption process. The discrepancies in these x values between the two extracts may signify differences in their molecular structures or surface-active components. Such insights further deepen our understanding of the adsorption mechanisms involved and highlight the distinct behaviors exhibited by the R.B.V.L and P.C.S extracts in inhibiting steel corrosion. Furthermore, the application of the Kinetic-thermodynamic model revealed important insights into the adsorption process. The values of 1/y and K provide valuable insights into the adsorption behavior of the R.B.V.L and P.C.S extracts, shedding light on both the number of active sites occupied by a single inhibitor molecule and the strength of interaction between the adsorbate and adsorbent, respectively. For the R.B.V.L extract, the 1/y value is 1.048, indicating that approximately one inhibitor molecule occupies each active site available for adsorption. Conversely, for the P.C.S extract, the 1/y value is 0.633, suggesting a lower occupancy of active sites per inhibitor molecule. This discrepancy may arise from differences in the molecular structure or surface-active components of the extracts. Furthermore, the higher K value obtained for the R.B.V.L extract (13.03) compared to the P.C.S extract (1.457) implies a stronger interaction between the R.B.V.L extract's active ingredients and the metal surface. This stronger interaction potentially enhances the effectiveness of the R.B.V.L extract as a corrosion inhibitor compared to P.C.S extract. Additionally, the negative values of ΔG_{ads} indicate the spontaneity of adsorption for both extracts. This suggests that the adsorption process occurs spontaneously and is favorable from a thermodynamic perspective. Moreover, the negative ΔG_{ads} values suggest a physisorption mechanism, where the adsorption is driven primarily by weak intermolecular forces such as Van der Waals interactions.

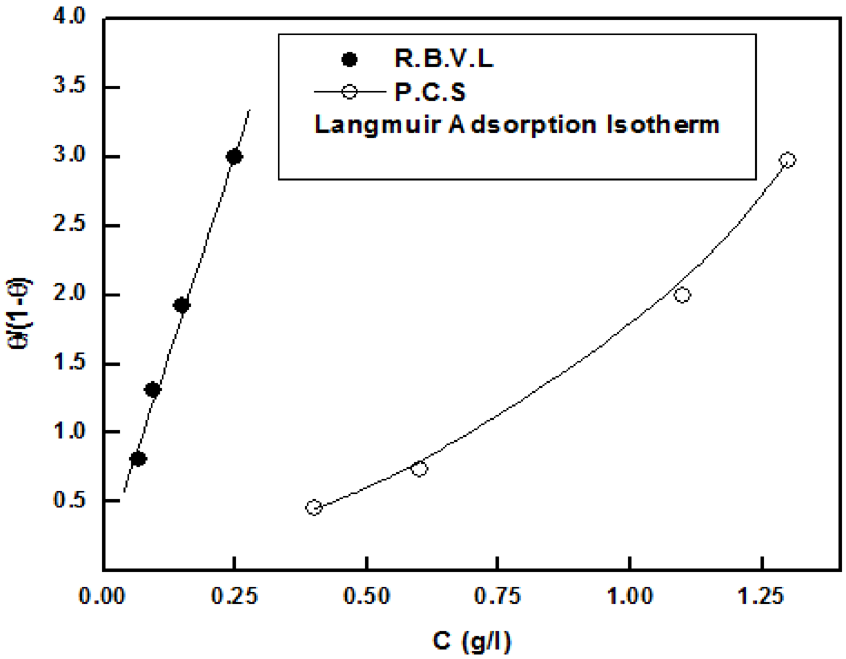


Fig. 9. Linear fitting of the experimental data to Langmuir adsorption Isotherm for R.B.V.L and P.C.S extracts

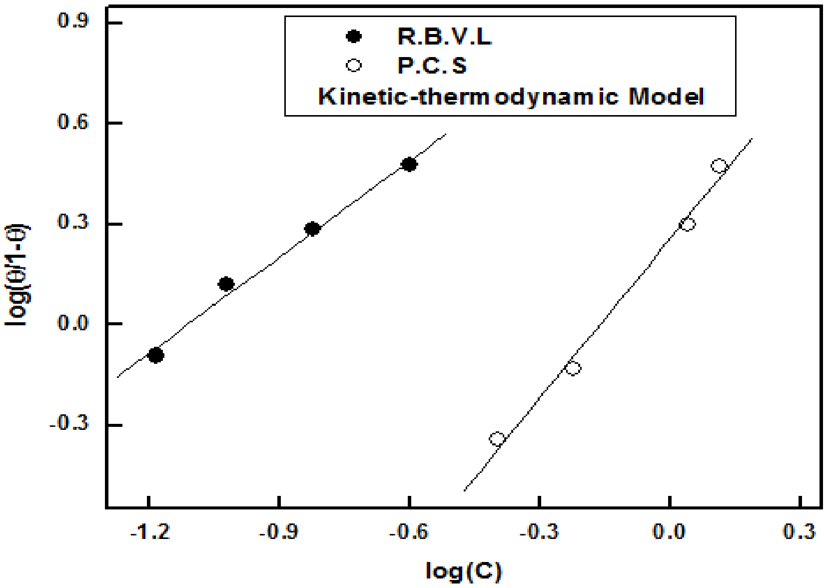


Fig. 10. Linear fitting of the experimental data to Kinetic-thermodynamic model for R.B.V.L and P.C.S extracts

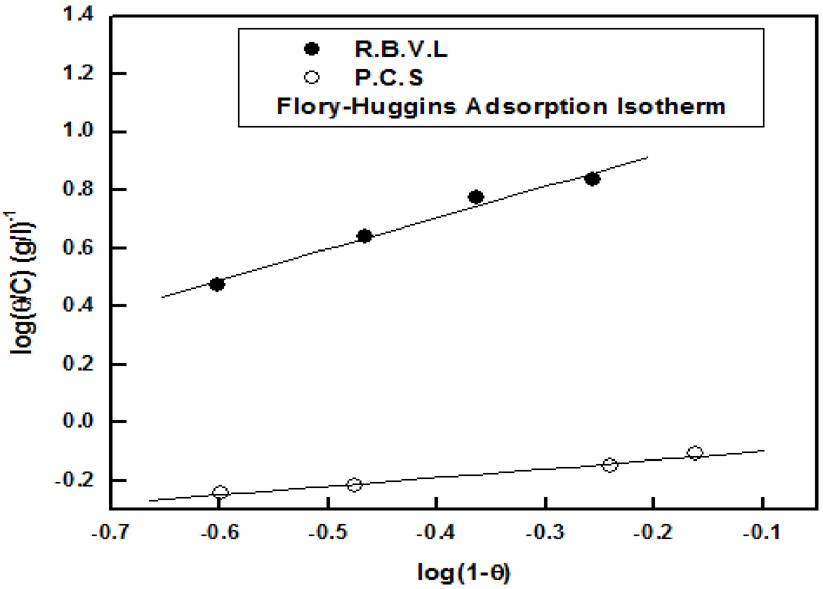


Fig. 11. Linear fitting of the experimental data to Flory-Huggins adsorption isotherm for R.B.V.L and P.C.S extracts

3.7 The Effect of Temperature

To assess the influence of temperature on the corrosion rate of steel, we employed the weight-loss method in the presence and absence of R.B.V.L and P.C.S extracts at concentrations of 0.250 g/L and 1.3 g/L, respectively. As depicted in Table 5, we observed a notable increase in weight loss with rising temperatures.

As the temperature increased, the corrosion rate exhibited a corresponding rise. This trend underscores the heightened reactivity of the corrosive environment with increasing thermal energy. The presence of R.B.V.L and P.C.S extracts demonstrates inhibition efficiencies across all temperature ranges, albeit with variations in corrosion rates. This observation suggests the potential of these extracts to mitigate corrosion even under elevated temperature conditions, highlighting their promising corrosion inhibition properties.

Table 5
Weight loss measurements of steel in 1.0 M HCl in the presence and absence of 0.250 g/L for R.B.V.L and 1.3 g/L for P.C.S extracts at a) 30, b) 40, c) 50, and d) 60 °C

R.B.V.L			P.C.S		
Conc., g/L	Rate, g/cm^3.hr	%η	Conc., g/L	Rate, g/cm^3.hr	%η
a) 0.00	0.0112	-	0.00	0.0112	-
0.25	0.00282	74.8	1.30	0.00284	74.6
b) 0.00	0.0120	-	0.00	0.012	-
0.25	0.0033	72.5	1.30	0.0033	72.5
c) 0.00	0.0126	-	0.00	0.0126	-
0.25	0.0037	70.6	1.30	0.0036	71.4
d) 0.00	0.0133	-	0.00	0.0133	-
0.085	0.004	69.9	0.6	0.0039	70.7

3.8 Quantum Chemical Calculations

The use of quantum calculations in corrosion inhibitor research has received a lot of interest in the recent decade. Because of its theoretical background, quantum calculation-based density function theory (DFT) is widely accepted as a "green corrosion inhibition technology". Using FT-IR and GC-MS techniques the chemical structures obtained from the two extracts are given in Table 7 and Table 8.

The energy of the highest occupied molecular orbital, lowest unoccupied molecular orbital, and energy gap (E_{HOMO}, E_{LUMO}, and, ($\Delta E = E_{HOMO} - E_{LUMO}$)) of various chemical structures of R.B.V.L. and P.C.S. extracts obtained using DFT with the B3LYP/6-31G(+) basis set in the aqueous phase are shown in Tables 6 and Table 7.

Table 6
E_{HOMO}, E_{LUMO}, and ΔE of R.B.V.L extract

Extract	Chemical structure	E_{HOMO}	E_{LUMO}	ΔE
R.B.V.L.	21 Acetoxy – 6 a, 11a dihydroxy- 16 a, 17a- propyl methylene dioxypregena – 1,4 – diene – 3,20-dione	-4.98186	-2.29583	2.68603
	tert-butyl m-phenol	-8.93486	-4.47491	4.45995
	Trichloroacetic acid, tetradecyl ester	-7.33973	-2.22426	5.11547
	Methyl 2, 4-tri decadiynoate	-7.63198	-2.5078	5.12418
	Octacosanol	-9.75719	-0.96832	8.78887

Table 7
E_{HOMO}, E_{LUMO}, and ΔE of P.C.S. extract

Extract	Chemical structure	E_{HOMO}	E_{LUMO}	ΔE
P.C.S.	D-verbenone	-4.13994	-3.31408	0.82586
	N-[24-Oxo-3alpha,7alpha,12alpha-tris(trimethyl siloxy)-5beta-cholan-24-yl]glycine methyl ester	-8.57023	-3.70701	4.86322
	Eicosanoic acid	-7.18435	-1.05363	6.13072

Since the binding constant obtained from the Kinetics-thermodynamic model for the extracts is arranged in the following order: R.B.V.L. > P.C.S. Furthermore, a smaller energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) also suggests a stronger adsorption bond**.**

As a result, by comparing this order with the values of ΔE for the various chemical structures of the extracts. It could be concluded that the active ingredients for R.B.V.L, and P.C.S are (21 Acetoxy – 6 a, 11a dihydroxy- 16 a, 17a- propyl methylene dioxypregena – 1,4 – diene – 3,20-dione), and Eicosanoic acid respectively as shown in Table 8.

The ionization potential (I) can be calculated using DFT-Koopmans' theorem as the negative of the highest occupied molecular orbital energy ($I = -E_{HOMO}$) [56]. The ionization potential value is the least amount of energy needed for electrons to attach to the surface of the metal and shield it from the corrosive medium. As a result, the low ionization potential (I) indicates the ease with which the atom can release its outer electron. It can donate electrons to the metal surface, thus increasing corrosion inhibition efficiency [57,58]. The data indicate that R.B.V.L. acts by shielding the surface via electron donation.

Table 8
Quantum chemical parameters (eV) for the optimized structure of chemical constituents of the extracts obtained using DFT with the B3LYP/6-31G(+).

		I	X	η	S
R.B.V.L.	21 Acetoxy – 6 a, 11a dihydroxy- 16 a, 17a- propyl methylene dioxypregena – 1,4 – diene – 3,20-dione	4.98186	3.63884	1.34302	0.74459
P.C.S.	Eicosonic acid	7.18435	4.1189	3.06535	0.32627

X signifies the absolute electronegativity of the inhibitor molecule (*X* = - ½[E_{HOMO}+E_{LUMO}]) *and η* denotes the absolute hardness of the inhibitor molecule (*η = ½* Δ*E)* [59,60]. High electronegativity values indicate that corrosion inhibitors are electron acceptors, while low ones indicate corrosion inhibitors as electron donors. This is because corrosion inhibitors with low electronegativity values will be easier to donate electrons or more reactive [61]. The electronegativity is lower than that of iron, 7 eV will donate its electrons to C.steel. Since the electronegativity of the chemical constituents of the extracts is lower than 7 eV. The inhibitive action of the active chemical constituents of the extracts takes place via electron donation by the conclusion mentioned previously [62–64].

The softness parameter, S, is the inverse of the hardness parameter that measures the softness of the inhibitor and thus its reactivity. The most effective metal corrosion inhibitors are those with the highest softness [65,66]. This is because a soft molecule (inhibitor) is more reactive towards a metal surface than a hard molecule (inhibitor) [67]. Thus, 21 Acetoxy – 6 a, 11a dihydroxy- 16 a, 17a-propyl methylene dioxypregena – 1,4 – diene – 3,20-dione with higher S but lower *I* and η is a better corrosion inhibitor. The tabulated quantum chemical parameters values suggest that the active chemical constituents of R.B.V.L extract may provide stronger inhibition compared to those of P.C.S. extract.

3.9 Mechanism of Inhibition

Analysis of the standard free energy of adsorption of the extracts, the temperature dependence of inhibition efficiency, and values of activation energies in the absence and presence of extracts provide some information about the possible mechanism of the extract adsorption. A decrease in the inhibition efficiency with the increase in temperature as well as the obtained values of ΔG_{ads} reveal that physisorption (electrostatic) is the mechanism by which the adsorption occurs [55]. In the presence of R.B.V.L and P.C.S extracts, the apparent activation energy (E_a) values increase, indicating the ability of extracts to reduce corrosion [68]. It is reported that the adsorption mechanism in acidic solutions is done by either the protonated species or the molecular form of the organic constituents. In hydrochloric acid solutions, the steel specimen has a positive surface charge [69]. So, protonated species should be poorly adsorbed. However, due to the specific adsorption of negative Cl^- ions in hydrochloric acid to the steel surface, the physical adsorption of the protonated form of the extracts to the steel surface becomes favored.

4. Conclusions

Both R.B.V.L and P.C.S extracts act as good eco-friendly corrosion inhibitors for B7-grade steel during acid pickling. The inhibition efficiency increases with both extracts' concentrations reaching inhibition efficiency roughly equal to 75 %. Corrosion activation energies were higher in the presence of the extracts, and temperature dependence of inhibition efficiency studies revealed that when the temperature increases, the inhibition efficiency decreases, suggesting a physisorption mechanism.

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