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Cinnamomum zeylanicum Extract as Green Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid Solutions

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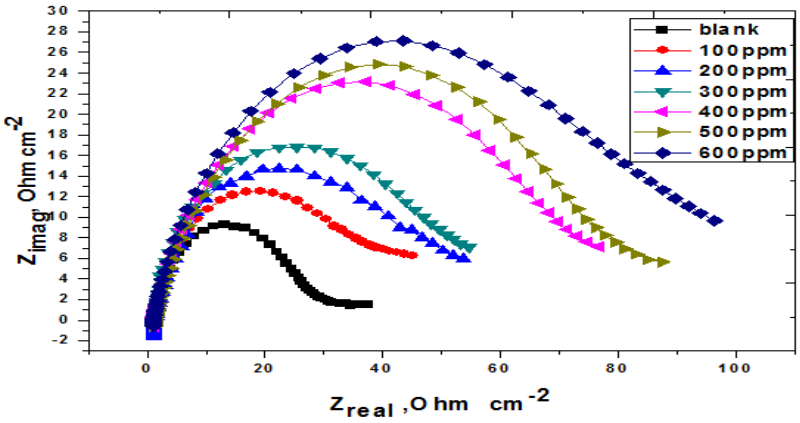
GRAPHICAL ABSTRACT



KEYWORDS

Corrosion
Cinnamomum
C-steel
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Green inhibitor

ABSTRACT

The extraction of cinnamomum have been evaluated as green inhibitor for the corrosion of carbon steel in 1M HCl solution was investigated using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (FEM) and energy dispersion spectroscopy (EDS) and scanning electron microscopy (SEM) methods of monitoring corrosion. The inhibitive property of the extraction is attributed to the presence of cinnamic aldehyde as major constituent in the extraction. Measurements showed that this extraction act as mixed-type inhibitor. The inhibition efficiency was found to increase with inhibitor concentration. Results obtained by various techniques are close to each other and maximum efficiency of 81.1 % is acknowledged at the inhibitor concentration of 600 ppm. Langmuir isotherm model is found most suitable to explain adsorption behavior of inhibitor for C-steel surface. Molecular adsorption of inhibitor over C- steel surface is found responsible for corrosion inhibition of C-steel in acid.

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1. Introduction

Corrosion inhibitors are chemical compounds usually used in small concentrations whenever a metal is in contact with an aggressive medium. The presence of such compounds retards the corrosion process and keeps its rate to a minimum and thus prevents economic losses due to metallic corrosion. The chemical compounds that could be used for this purpose may be organic or inorganic. However, not just any chemical compound can be used as a corrosion inhibitor. There are some requirements that the compound must fulfill to do so. Regarding the chemical structure and chemical behavior, an inorganic compound must be able to oxidize the metal, forming a passive layer on its surface. On the other hand, a molecule of an organic compound must have some features that give it the ability to act as a corrosion inhibitor. Among these, the molecule may have a large structure, double bonds, an active center or group, etc. These features give the molecule the ability to cover a large area of a metal surface with a firmly attached film[1].

Apart from the structural aspects, there are also economic and environmental considerations. Thus, since the whole subject of corrosion is about its destructive economical effect, the used inhibitor must be cheap. Furthermore, due to the recent increasing awareness of green chemistry, it must be a nontoxic and environmentally friendly chemical. One of the sources of these cheap and clean inhibitors is plants. Plant parts contain several compounds that satisfy the mentioned criteria. Many recent researches have adopted this trend and carried out their work on naturally occurring substances[2-9].

Promising results were obtained in previous work in this field. It was reported that Khillah extract inhibits steel corrosion in HCl solution with inhibition efficiency (%IE) as high as 99% [2], while opuntia extract inhibits the corrosion of aluminum in the same acid with efficiency of about 96% [1].

The aim of this work is to study the effect of using extract of cinnamomum as green inhibitor for the corrosion of C-steel in 1M HCl using weight loss method (chemical method) and the electrochemical techniques such as potentiodynamic polarization measurements, electrochemical impedance spectroscopy (EIS) techniques and electrochemical frequency modulation method.

2. Materials and Methods

Protein Sequence Extraction

The experiments were performed with C- steel specimens in the form of rods and sheets with the following composition (weight %):0.200 % C, 0.350 % Mn, 0.024 % P, 0.003 % S, and the remainder Fe. For electrochemical measurements, the sheets were welded with Cu-wire for electrical connection and mounted into glass tubes of appropriate diameter using Araldite to offer an active surface of 1 cm2 geometric area, to contact the test solution. Prior to each experiment, these sheets were polished with emery paper (400-1000 grade) to a mirror finish and degreased with trichloroethylene, washed with distilled water and then dried. A conventional electrochemical cell of capacity 100 ml was used containing three compartments for C- steel as working electrode, platinum foil with a 1 cm^2 surface area was chosen as the counter electrode and saturated calomel electrode (SCE) via a Luggin capillary probe was used as the reference. All reagents used (HCl) for this study was of analytical grade and were used as received and distilled water was used for their preparations. All experiments were carried out open to the atmosphere. The experiments were repeated and reproducibility was tested and confirmed.

2.2. Cinnamomum extraction

This seeds are very popular in world and used in many regions. Seeds of this plant contain many organic

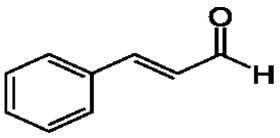
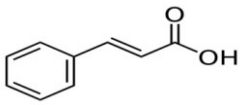
compounds as cinnamic aldehyde [10-12]. This seeds is selected for the study due to simple extraction method, non toxic nature, low cast and presence of effective organic compounds which contain C and O heteroatoms, -CO group and π electrons in their structure. Although crude extract is used in this study for simplicity and effective cost but we are working on purification of the extract to enhance the inhibition efficiency at low concentration.

Fresh seeds were bought from the local market and washed with double distilled water. Seeds were cut and dried at 40˚C for two days. Powdered form of seeds was obtained using grinder and distilled water was added to make a solution. This solution was kept at room temperature for two days with constant stirring. Further extract was filtered and water was evaporated using rotary evaporator. Solid residue obtained by this process was again dissolved in 100 mL distilled water and stock solution was prepared.

2.3 Weight loss method

The samples measuring 2 x 2 x 0.2 cm were prepared as before. The specimens were immersed in 250 ml beaker, which contained 100 ml of 1 M HCl with and without different concentrations of inhibitors.

Table 1. Molecular structures and names of main components in Cinnamomum extract.

Chemical Constituents	Structure	IUPAC
Cinnamic aldehyde		(2E)-3-phenylprop-2-enal
Cinnamic acid		(E)-3-phenylprop-2-enoic

After 3 h, the specimens were taken out, washed, dried, and weighed accurately. The average weight loss of the parallel C-steel sheets could be obtained. Then the tests were carried out at a temperature range 25–55˚C. The inhibition efficiency (IE) of the inhibitor and corrosion rate (CR) in mg cm^{-2} min^{-1} of C-steel in HCl solution were calculated using equations (1) and (2) respectively [13]:

$$\% IE=[1-(W_1/W_2)]x\ 100 \quad (1)$$

$$CR=[W_2-W_1]/At \quad (2)$$

Where W_1 and W_2 are the weight losses (mg cm^{-2}) in the presence and absence of the extract, respectively, A is the area of the specimen in cm^{-2} and t is the period of immersion in min.

2.4 Potentiodynamic polarization measurements

Before polarization scanning, working electrode was immersed in the test solution (100 ml) for 30 min until steady state was attained this was taking as EOC. All experiments were carried out at 25 ± 1˚C and solutions were not aerated. For polarization measurements potential from -300 to 100 mV [relative to open circuit potential, (EOCP)] was applied. The inhibition efficiency was calculated using equation (3):

$$\% IE = [1- (i_{corr(inh)} / i_{corr(free)})] \times 100 \quad (3)$$

Where $i_{corr(free)}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of extract, respectively.

2.5 Electrochemical impedance spectroscopy method

The EIS spectra were recorded at OCP after immersion of the electrode for 30 min in the test solution in order to attain steady state. The AC signal was 5 mV peak to peak and the frequency range studied was between 100 kHz and 0.2 Hz.

The % IE and the surface coverage (θ) of the used inhibitors obtained from the impedance measurements can be calculated using equation (4):

$$\%IE=\theta x100=[1-(R^{\circ}_{ct}/R_{ct})]\times 100 \quad (4)$$

R°_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor, respectively

2.6 Electrochemical frequency modulation (EFM)

Electrochemical frequency modulation was carried out using two frequencies i.e. 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1s. The Intermodulation spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density (i_{corr}), the TOFEL slopes (β_c and β_a) and the causality factors CF-2& CF-3 [14, 15]. All electrochemical experiments were carried out using Potentiostat/Galvanostat/Zra analyzer (Gamry PCI300/4). A personal computer with DC 105 software for polarization, EIS 300 software for impedance, EFM140 software for electrochemical frequency modulation and Echem Analyst 5.21 was used for data fitting and calculating.

3. Results and Discussion

3.1 Weight loss measurements

The weight loss-time curves of C-steel specimens in 1 M HCl solution, with and without different concentrations from the investigated cinnamomum extract, were determined after 3h of immersion at 25°C which are given in Fig. 1. The IE percent are given in Table 2. The presence of inhibitor reduces the corrosion rate of C-steel in HCl. From the plot, weight loss for systems was found to be lower compared to the blank indicating that different concentrations of cinnamomum extract retard the corrosion of C-steel in 1 M HCl. The Figure reveals that the inhibitor (plant extraction) actually inhibited the HCl corrosion of C-steel to an appreciable extent. The Figure also reveals that C-steel corrosion in HCl occurs not by simple homogenous process but by a heterogeneous one consisting of different or same rates.

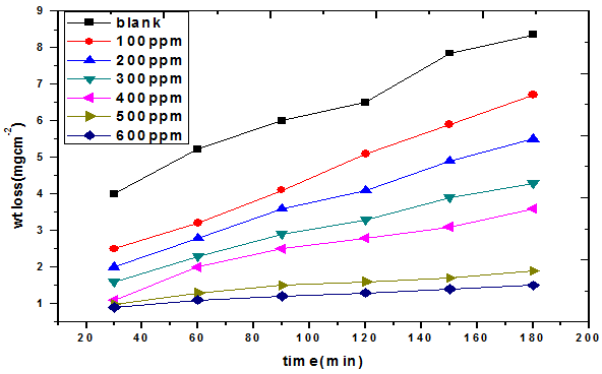


Fig. 1. Weight loss-time curves for the corrosion of C-steel in 1 M HCl in absence and presence of different concentrations of Cinnamomum extract at 25°C

This assertion is made from the non-uniformity or nonlinearity of the plots obtained [16].

3.2. Adsorption isotherm and thermodynamics parameters

The mechanism of the interaction between inhibitor and the metal surface can be explained using adsorption isotherms.

Assuming direct relationship between surface coverage and inhibition efficiency, the degree of surface coverage, θ, was computed for the different concentrations of the extract from weight loss measurements as follows:

$$\%\ IE = 100\ \theta$$

The surface coverage values obtained were applied to various adsorption isotherm models. By far, the best equation was found to obey Langmuir adsorption isotherm (Fig. 2), which is formulated as in equation (5):

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

Where, K_{ads} is the adsorption equilibrium constant of the inhibitor, C is the inhibitor concentration and θ is the surface coverage. The free energy of adsorption (ΔG°_{ads}) can be obtained from equation (6):

$$\log K_{ads} = -\log 55.5 - \Delta G^{\circ}_{ads}/ 2.303RT \quad (6)$$

Where, R is the universal gas constant, T is the absolute temperature, the value 55.5 is the concentration of water on the metal surface in mol/L.

Table 2. Weight loss measurements for C-steel in 1 M HCl in the absence and presence of different concentrations of cinnamomum extract at a temperature range (25-55 °C).

Temperature	Conc., ppm	Weight loss, mg/cm²	Θ	% IE
25 °C	Blank	6.50	--	--
	100	4.5	0.308	30.8
	200	4.1	0.369	36.9
	300	3.3	0.492	49.2
	400	2.8	0.569	56.9
	500	1.6	0.754	75.4
	600	1.3	0.8	80.0
35 °C	Blank	11.16	--	--
	100	7.8	0.301	30.1
	200	7.2	0.355	35.5
	300	5.83	0.478	47.8
	400	4.86	0.565	56.5
	500	4.32	0.613	61.3
	600	3.88	0.652	65.2
45 °C	Blank	28.45	--	--
	100	20.1	0.293	29.3
	200	18.1	0.349	34.9
	300	15.1	0.469	46.9
	400	12.8	0.55	55.0
	500	11.2	0.606	60.6
	600	9.98	0.649	64.9
55 °C	Blank	57.34	--	--
	100	41.1	0.288	28.8
	200	30.8	0.462	46.2
	300	29.1	0.494	49.4
	400	25.1	0.564	56.4
	500	23.3	0.599	59.9
	600	21.2	0.634	63.4

The negative values of ΔG°_{ads} in Table 3 suggested that the adsorption of inhibitor molecules onto C-steel surface is a spontaneous process. Generally, values of ΔG°_{ads} up to -20 kJ mol^{-1} are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than -40 kJ mol^{-1} involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [17, 18].

The large K_{ads} value gives better inhibition efficiency due to strong electrical interaction between the double layer and adsorbing inhibitor molecules while a small K_{ads} value

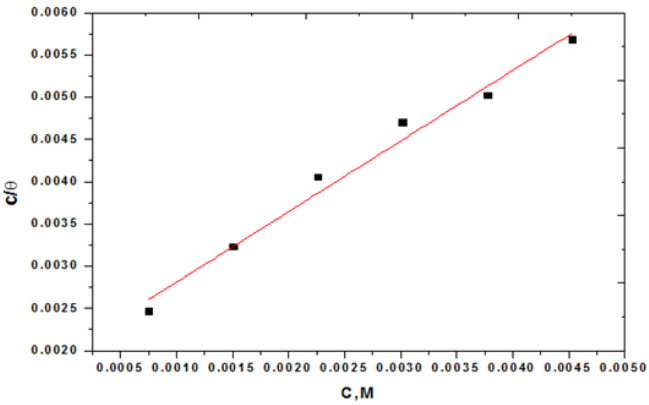


Fig. 2. Adsorption isotherm on C-steel in 1M HCl at 25°C

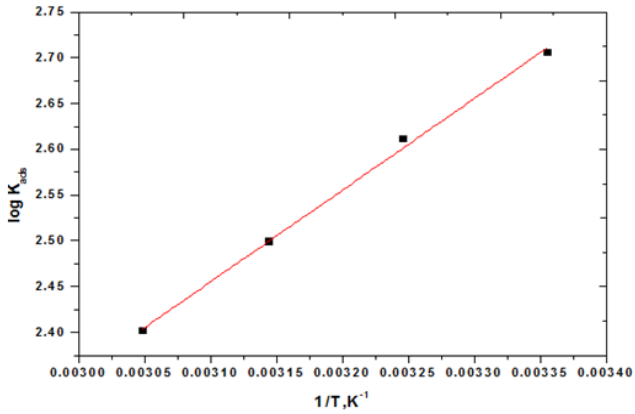


Fig. 3. Variation of log K_{ads} with 1/ T

compromise that such interactions between the adsorbing inhibitor molecules and the metal surface are weaker, indicating that the inhibitor molecules are easily removable by the solvent molecules from the surface of C-steel.

Figure 3 shows the plot of log K_{ads} vs. 1/ T, a straight line with an intercept equal to ΔH°_{ads} and with slope equal to ΔS°_{ads} in Equation (7):

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad (7)$$

The negative sign of ΔH°_{ads} indicated that the adsorption of inhibitor molecules is an exothermic process in all cases. The sign of ΔS°_{ads} is negative because inhibitor molecules freely moving in the bulk solution were adsorbed in an orderly fashion on to C-steel, resulting in a decrease in entropy [19]. Moreover, from thermodynamic principles, since the adsorption was an exothermic

process, it must be accompanied by a decrease in entropy [20].

3.3- Effect of temperature

Temperature plays an important role on metal dissolution. The corrosion rate in acid solution, for example, increases exponentially with temperature increase because the hydrogen evolution overpotential increases [21].

In order to access the effect of temperature on the corrosion and corrosion inhibition process, weight loss experiments were carried out in the temperature range 25-55°C in 1 M HCl in the absence and presence of different concentrations (100-600 ppm) of Cinnamomum extract.

Table 3. Thermodynamic parameters for C-steel in 1 M HCl for cinnamomum extract.

Temp. K	$-\Delta S^{\circ}_{ads}$ J mol^{-1}K^{-1}	$-\Delta H^{\circ}_{ads}$ kJ mol^{-1}	$-\Delta G^{\circ}_{ads}$ kJ mol^{-1}	K_{ads} X 10^{+3} M^{-1}
298	20.89	19.16	25.39	5.08

It was found that after 3 h immersion period, the surface coverage and inhibition efficiency decrease with rise in temperature Table 2. Arrhenius-type dependence is observed between corrosion rate and temperature often expressed as in equation 8:

$$\text{Corrosion Rate (CR)}=A \exp - E_a^*/RT \quad (8)$$

Where CR is the corrosion rate, E_a^* is the apparent activation energy, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor. Figure 5 depicts an Arrhenius plot (logarithm of CR against the reciprocal of temperature (1/T) for C-steel in 1 M HCl solution in the absence and presence of different extract concentrations. Satisfactory straight lines of high correlation coefficients were obtained. The values of activation energy were obtained from the slopes of the linear plots and are given in Table 3. It is clear that E_a^*values in the presence of the different concentrations of the extract are higher than in their absence. The higher in apparent activation energy in the presence of the extract denotes physical adsorption while the reverse is usually attributed to chemical adsorption [22]. This conclusion is denoted by the decrease in inhibition efficiency with increasing temperature (Table 2). Similar result has been reported by Okafor et al. [23] on the inhibition of acid corrosion of carbon steel using aqueous extract of P. amarus seeds and leaves. Moreover, the increase in activation energy is proportional to the inhibitor concentration, indicating that the energy barrier for the corrosion process is also increased [24]. An alternative formulation of Arrhenius equation is [25]:

$$CR=(RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \quad (9)$$

Where h is the Planck's constant and N is the Avogadro's number, ΔS^* is the entropy of activation, and ΔH^* is the enthalpy of activation. Figure 6 shows a plot of Log (CR/T) as a function of 1/T. Straight lines were obtained with a slope of (ΔH^*/ R) and an intercept of (lnR/ Nh - ΔS^*/R) from which the values of $\Delta H^*$and ΔS^*were calculated Table 4. The positive values of ΔH^* both in the absence and presence of the extract reflect the endothermic nature of the C-steel dissolution process. It is also clear that the activation enthalpies vary in the same manner as the activation energies, supporting the proposed inhibition mechanism.

Table 4. Kinetic activation parameters for C-steel in 1M HCl in the absence and presence 300 ppm Cinnamomum extract

Inhibitors	Conc. ppm	Activation parameters		
		E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1}K^{-1}
Blank	0.0	42.02	20.98	155.29
Extract	300	56.04	53.72	95.02

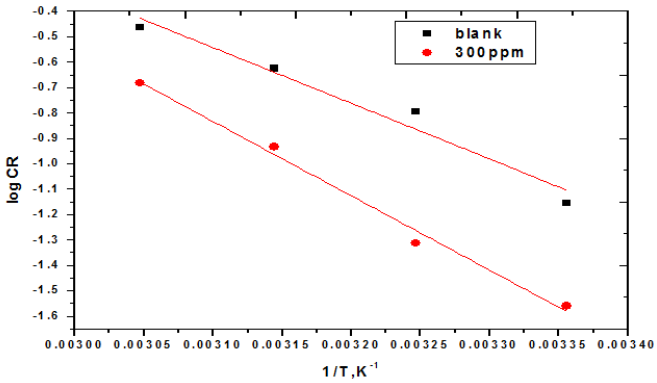


Fig. 4. Arrhenius plot of variation of (log CR) vs. (1/T) for dissolution of C-steel in 1M HCl in absence and presence of 300 ppm of Cinnamomum extract.

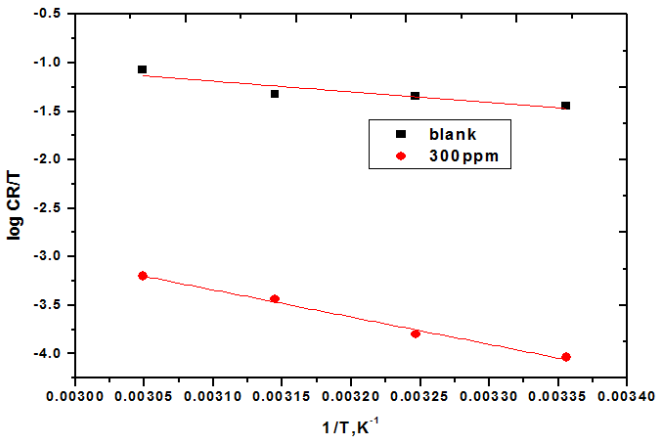


Fig. 5. Arrhenius plot of variation of (log CR/T) vs. (1/T) for dissolution of C-steel in 1M HCl in absence and presence of 300 ppm of Cinnamomum extract.

Large and negative values of entropies imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. Similar observation has been reported in the literature [25].

3.4 - Potentiodynamic polarization measurements

Potentiodynamic polarization curves for C-steel in uninhibited and inhibited acidic solutions containing different concentrations of cinnamomum extract are shown in Fig.6. The corrosion kinetic parameters derived from potentiodynamic polarization curves together with % IE are listed in Table 4. It has been observed that values of corrosion current density (i_{corr}) for C-steel in 1 M HCl solution decreased with increase in Cinnamomum extract concentration. The decrease in corrosion current densities in the presence of inhibitor might be due to the adsorption of Cinnamomum extract components molecules on the C-steel surface. In the absence and presence of Cinnamomum extract, β_a and β_c values remain more or less identical indication that the effect of extract is not as large as to change the mechanism of corrosion. The value of corrosion potential ($E_{corr.}$) showed a slight shift towards anodic region as concentration of extract increased, suggesting the effect of extract is more pronounced at anodic site. It was reported before [26] that, if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of uninhibited solution, the inhibitor can be seen as a cathodic or anodic type. In our study the maximum displacement was 15 mV, indicating that Cinnamomum extract belonged to mixed-type.

3.5 Electrochemical impedance spectroscopy (EIS)

The corrosion of C-steel in 1 M HCl in the presence of Cinnamomum extract was investigated by EIS method at 25 ºC. Impedance parameters, such as, charge transfer resistance R_{ct}, which is equivalent to R_p, and the double layer capacitance C_{dl} are derived from the Nyquist plot (Fig. 7) and are given in Table 6 for C-steel in 1M HCl acid solution in the presence and absence of the extract. It is observed that the values of R_{ct} increase with increasing the concentration of the extract and this in turn leads to a decrease in corrosion rate of C-steel in 1M HCl acid solution. Impedance diagram have a semicircular appearance; the diagram indicate that the corrosion of C-steel is mainly controlled by a charge transfer process [27]. The values of double layer capacitance, C_{dl}, decrease with increasing the concentration of Coffee extraction. A low capacitance may result if water molecules at the electrode interface are replaced by inhibitor molecules of lower dielectric constant through adsorption.

Table 5. Corrosion parameters obtained from potentiodynamic polarization of C-steel in 1M HCl containing various concentrations of Cinnamomum extract at 25°C

Comp.	Conc, ppm	$-E_{corr}$, mV vs.SCE	i_{corr} mA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	θ	% IE	CR mpy
Blank	0.0	449	959.0	236.0	159.8	-	-	252.9
Cinnamon extract	100	462	349.1	159.3	94.6	0.636	63.6	154.9
	200	481	334.2	147.4	97.1	0.652	65.2	152.8
	300	483	292.4	154.4	108.9	0.696	69.6	133.8
	400	489	258.6	158.9	129.3	0.731	73.1	118.0
	500	490	220.8	162.7	134.4	0.771	77.1	100.5
	600	496	181.2	164.0	123.4	0.811	81.1	82.7

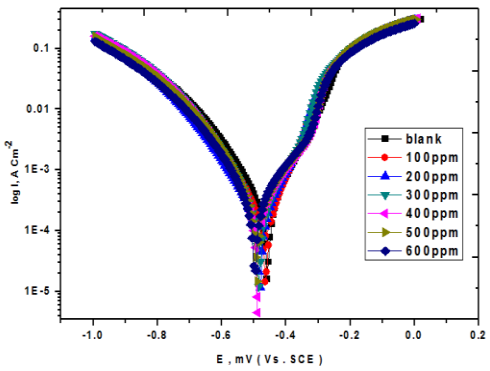


Fig. 6. Potentiodynamic polarization curves of C-steel in 1 M HCl in the absence and presence of different concentrations of Cinnamomum extract at 25°C

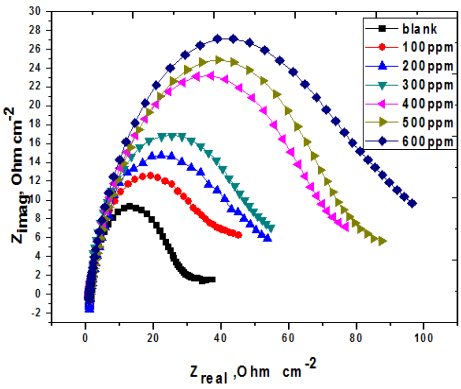


Fig. 7. Nyquist plot of C-steel in 1 M HCl in the absence and presence of different concentrations of Cinnamomum extract at 25°C

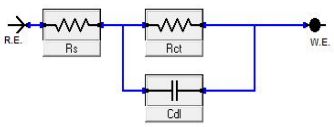


Fig. 8. Equivalent circuit model used to fit impedance data

Table 6. EIS data of C-steel in 1 M HCl and in the presence and absence of different concentrations of Cinnamomum extract at 25°C

Comp.	Conc., ppm	C_{dl}, μF cm^{-2} cm^{-2}	R_{CT}, Ω cm^2	θ	%IE_{EIS}
Blank	0.0	132.4	28.5	-	-
Cinnamon extract	100	109.2	40.4	0.295	29.5
	200	96.6	51.9	0.451	45.1
	300	82.5	58.6	0.514	51.4
	400	76.9	72.6	0.606	60.6
	500	68.2	84.9	0.664	66.4
	600	60.1	105.9	0.439	73.9

When such low capacitance values in connection with high R_{ct} values, it is apparent that a relationship exists between adsorption and inhibition. The impedance data of C-steel in 1 M HCl are analyzed in terms of an equivalent circuit model (Fig. 8) which includes the double layer capacitance C_{dl} which is placed in parallel to the charge transfer resistance R_{ct} [28] due to the charge transfer reaction. C_{dl} can be calculated from the angular frequency ($\omega = 2\pi f$) at the maximum imaginary component and the charge transfer resistance according equation 10:

$$C_{dl} = [1/\omega_{max} R_p] = [1/2\pi f_{max} R_p] \quad (10)$$

Where f is maximum frequency, ω is the angular velocity.

3.6. Electrochemical Frequency modulation (EFM)

The EFM is a non-destructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of TAFEL constants. Like EIS, it is a small AC signal. Inter-modulation spectra obtained from EFM measurements are presented in Figures 9 and 10 as examples of C-steel in aerated 1 M HCl and containing different concentrations of cinnamomum at 25°C. Each spectrum is a current response as a function of frequency. The calculated corrosion kinetic parameters at different concentrations of coffee extract in 1 M HCl at 25°C (i_{corr}, β_a, β_c, CF-2, CF-3 and % IE) are given in Table 7.

From Table 7, the corrosion current densities decrease by increasing the concentration of cinnamomum and the inhibition efficiency increases by increasing the extract concentration. The causality factors in Table 7 are very close to theoretical values (2.0 & 3.0) which according to EFM theory should guarantee the validity of TAFEL slopes and corrosion current densities and indicate that the measured data are of good quality. The deviation of causality factors from their ideal values might be due to the perturbation amplitude was too small or the resolution of the frequency spectrum is not high enough also another possible explanation that the inhibitor is not performing very well. The obtained results showed good agreement of inhibition efficiency obtained from the potentiodynamic polarization, EIS and weight loss methods.

The EDS spectra were used to determine the elements present on the surface of C-steel and after 3 days of exposure to the uninhibited and inhibited 1M HCl.

Table 6. Electrochemical kinetic parameters obtained from EFM technique for C-steel in the absence and presence of various concentrations of Cinnamomum extract in 1M HCl at 25˚C

Comp.	Conc., ppm	i_{corr}, μAcm^{-2}	β_c, $mVdec^{-1}$	β_a, $mVdec^{-1}$	CF-2	CF-3	θ	%IE	CR, mmy^{-1}
Blank	00	628.1	126.3	98.7	1.940	2.978	----	----	287.1
Cinnamon extract	100	448.8	113.5	97.6	1.903	3.021	0.2855	28.55	205.1
	200	373.2	129.9	101.7	1.969	3.301	0.4058	40.58	170.5
	300	318.8	139.2	102.9	2.036	2.989	0.4924	49.24	165.2
	400	298.4	135.2	121.7	1.968	2.913	0.5249	52.49	148.6
	500	210.9	140.2	114.9	1.997	3.012	0.6642	66.42	141.7
	600	150.9	134.4	122.7	2.012	2.914	0.7598	75.98	120.3

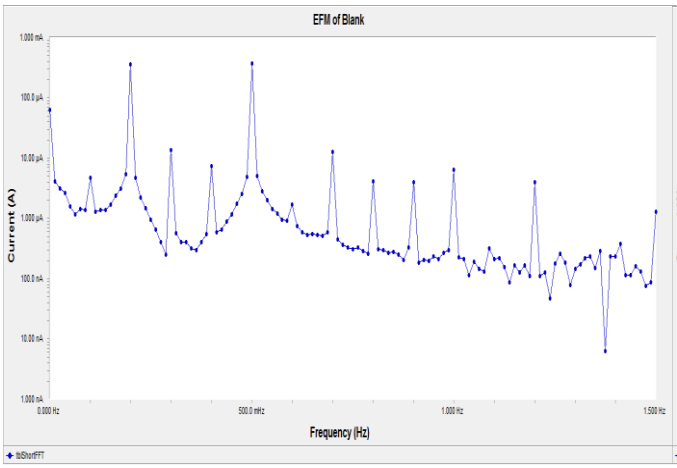


Fig. 9 EFM spectra for C-steel in 1M HCl (blank) at 25°C

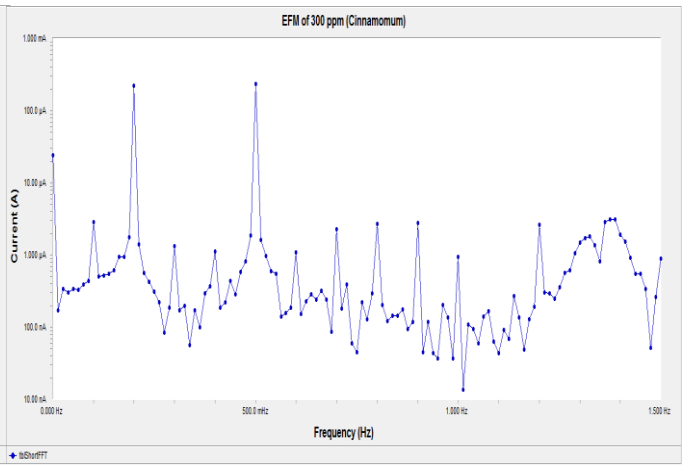


Fig. 10 EFM spectra for C-steel in 1M HCl solutions in the presence of 300 ppm Cinnamomum extract at 25°C

Fig. 11 shows the EDS analysis result on the composition of C-steel only without the acid and inhibitor treatment.

The EDS analysis indicates that only Fe and oxygen were detected, which shows that the passive film contained only Fe_2O_3. Fig.11 portrays the EDS analysis of C-steel in 1M HCl only and in the presence of 600 ppm of extract. The spectra show additional lines, demonstrating the existence of C (owing to the carbon atoms of Cinnamomum extract). These data shows that the carbon and O materials covered the specimen surface. This layer is entirely owing to the inhibitor, because the carbon and O signals are absent on the specimen surface exposed to uninhibited HCl.

It is seen that, in addition to Mn, O, and C were present in the spectra. A comparable elemental distribution is shown in Table 7.

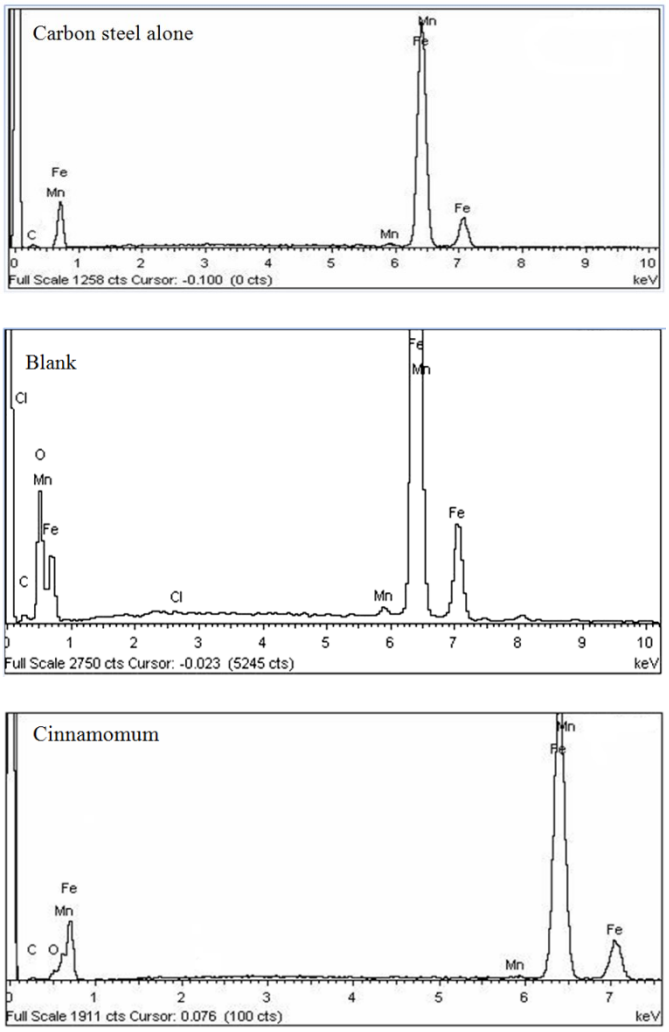


Fig.11 EDS analysis on C-steel in presence and absence of 600ppm Cinnamomum extract for 3 days immersion.

Table 7. Surface composition (wt%) of C-steel alloy after 3days of immersion in HCl without and with 600ppm of Cinnamomum extract

(Mass %)	Fe	Mn	C	O	N	Cl
carbon steel alone	96.78	0.61	4.87	--	--	--
Blank	55.83	0.31	2.12	39.24	--	0.32
Cinnamomum extract	59.42	0.40	18.15	10.98	--	-

3.8 Scanning Electron Microscopy (SEM) Studies

Fig. 12 represents the micrography obtained of C-steel samples after exposure to 1M HCl for three days immersion. It is clear that C-steel alloy surfaces suffer from severe corrosion attack.

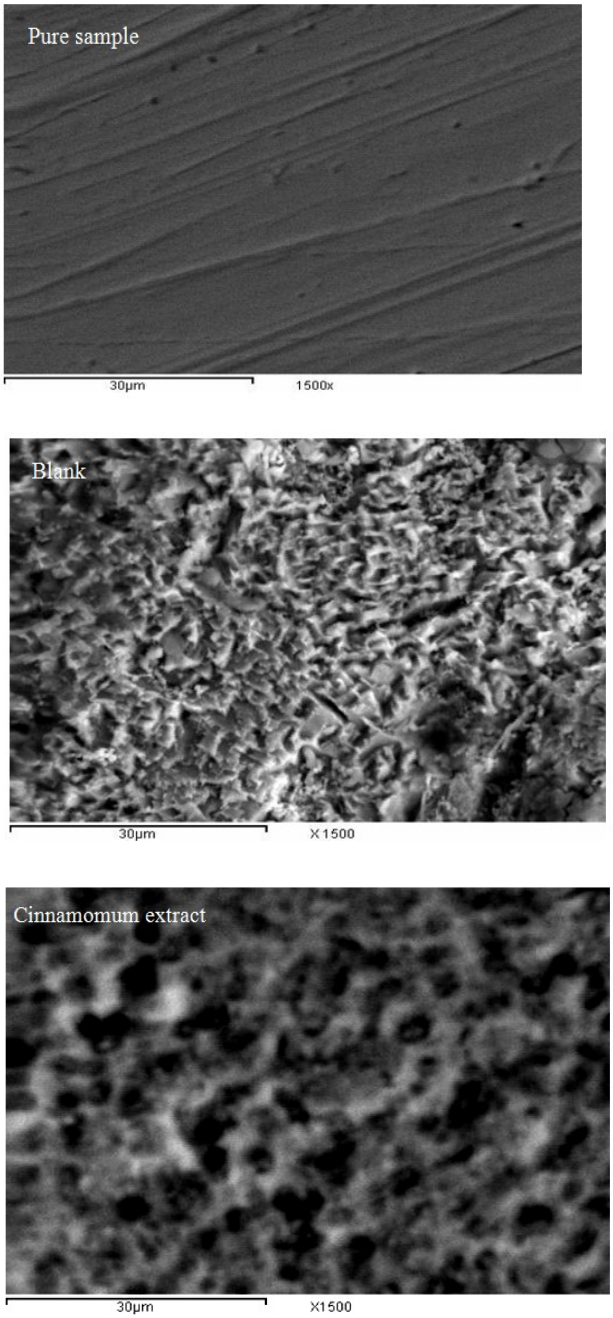


Fig. 12 SEM micrographs for C-steel in absence and presence of 600ppm of Cinnamomum extract

Fig. 12 reveals the surface on C-steel alloy after exposure to 1M HCl solution containing 600ppm of Cinnamomum extract.

It is important to stress out that when the compound is present in the solution, the morphology of C-steel alloy surfaces is quite different from the previous one, and the specimen surfaces were smoother. We noted the formation of a film which is distributed in a random way on the whole surface of the C-steel alloy.

This may be interpreted as due to the adsorption of Cinnamomum extract on the C-steel alloy surface incorporating into the passive film in order to block the active site present on the C-steel alloy surfaces. Due to the involvement of inhibitor molecules in the interaction with the reaction sites of C-steel alloy surface, resulting in a decrease in the contact between C-steel alloy and the aggressive medium and sequentially exhibited excellent inhibition effect.

3.9. Mechanism of corrosion inhibition

Corrosion of mild steel in HCl was found inhibited in presence of inhibitor. From analysis of the results obtained by various techniques it was recognized that changing surface property of steel with concentration of inhibitor was responsible for retarded corrosion rate which corresponds to molecular adsorption of inhibitor over mild steel surface. It is well known fact that most of the inhibitors falls under the category of adsorption type inhibitors and inhibit the corrosion by getting absorbed on the surface [29]. The organic species probably became protonated in acid solution which favored adsorption of these molecules over surface of negatively charged mild steel (electrostatic bonding) [30]. Adsorption of Cl- over mild steel surface produced unbalanced negative charge which promoted adsorption of inhibitor molecules at most active sites and inhibition efficiency was enhanced due to synergistic effect. Also these organic compounds contain C, and O heteroatoms, fused benzene rings and CO groups in their chemical structure which contributed electrons for sharing with vacant d orbit electrons of iron (chemi adsorption).

On the basis of facts discussed above it can be said that corrosion inhibition greatly depends upon adsorption of inhibitor molecules over surface of mild steel. In our case adsorbed inhibitor molecules accumulated at the metal/acid interface and constructed a layer surrounding mild steel. This layer prevented mild steel from further being corroded.

4. Conclusions

Based on the above results, the following conclusions can be drawn: Aqueous extract of Cinnamomum extract was found to be an efficient inhibitor for the corrosion of C-steel in 1 M HCl. Inhibition efficiency increased with an increase in Cinnamomum extract content in 1 M HCl but decreased with rise in temperature. The corrosion process is inhibited by adsorption of the Cinnamomum extract on the C-steel surface following the Langmuir adsorption isotherm. This indicates that the inhibition effect of the extract is due to adsorption of some or all the listed phytochemical constituents. Adsorption of aqueous extract of Cinnamomum extract on the surface of the C-steel is spontaneous and occurs by physical adsorption. The negative free energy ($-\Delta G°_{ads}$) of adsorption indicates strong and spontaneous adsorption of the Cinnamomum extract on the C-steel surface. Values of TAFEL constants β_a and β_c confirm that the Cinnamomum extract acts like mixed type inhibitor. Increase in R_{ct} values and decrease in i_{corr} and Cd_l values confirm that the Cinnamomum extract is adsorbed on the mild steel surface and inhibition process is followed by monolayer adsorption. The inhibition efficiencies determined by mass loss and electrochemical methods are in reasonable good agreement. Thus the Cinnamomum extract was proved to be an effective eco friendly and low cost inhibitor [31, 32].

Conflict of interest

The authors declare that they have no competing interests.

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