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Capsicum extract as green corrosion extract for carbon steel in hydrochloric acid solutions

ABSTRACT

The extract of Capsicum have been evaluated as green extract for the corrosion of carbon steel in 1M HCl solution was investigated using weight loss, potentiodynamic polarization, ac 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 extract is attributed to the presence of Capsaicin and Ascorbic acid as major constituent in the extract. Measurements showed that this extract act as mixed-type extract. The inhibition efficiency was found to increase with extract concentration. Results obtained by various techniques are close to each other and maximum efficiency of 86 % is acknowledged at the extract concentration of 300 ppm. Langmuir isotherm model is found most suitable to explain adsorption behavior of extract for C-steel surface. Molecular adsorption of extract over C- steel surface is found responsible for corrosion inhibition of C- steel in acid.
Keywords: Corrosion inhibition, Capsicum extract, C- steel, HCl.

1. INTRODUCTION

Corrosion extracts 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 extract. 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 extract. Among these, the molecule may have a large structure, double bonds, an active center or group, etc.

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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 extract 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 extracts is plants. Plant parts contain several compounds that satisfy the mentioned criteria. Many recent researches [2–9] have adopted this trend and carried out their work on naturally occurring substances. 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 as high as 99% [2], while opuntia extract inhibits the corrosion of aluminum in the same acid with efficiency of about 96% [9].

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

2. EXPERIMENTAL

2.1. Materials

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 cm^2 geometric area, to contact the test solution. Prior to each experiment, these sheets were polished with emery paper (400-1200 grit size) to a mirror finish and degreased with trichloroethylene, washed with bidistilled 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 bidistilled 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. Test solution

Capsicum is very popular in world and used as vegetable in many regions. The extract of this plant contains many organic compounds as flavonoids, ascorbic acid, phenolic acids, polysaccharide and capsaicin [10-12]. This plant is selected for the study due to simple extraction method, non toxic nature, low cast and presence of effective organic compounds which contain N, O heteroatoms, -OH group and π electrons in their structures (fig.1). 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 fruits were bought from the local market and washed with bidistilled water. Fruits were cut and dried at 40°C for two days. Powdered form of fruits was obtained using grinder and bidistilled 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 rotatory evaporator. Solid residue obtained by this process was again dissolved in 100 mL bidistilled water and stock solution was prepared.
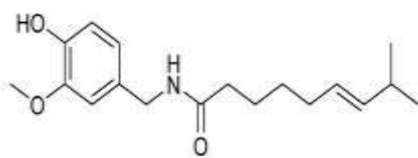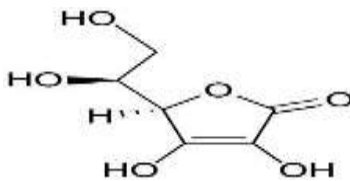
Chemical Constituents	Structures	IUPAC names
Capsaicin		Methyl-N-vanillyl-trans-6-nonenamide
Ascorbic acid		R)-3,4-dihydroxy-5-((S)- 1,2-dihydroxyethyl)furan-2(5H)-one

Figure 1 - Molecular structures and names of main components in Capsicum extract

2.3. Methods

2.3.1. Weight loss Measurements

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 extract. 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 ºC. The inhibition efficiency (IE), surface coverage (Ө) of the extract 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]:

$$\% \ IE = Ө \times 100 = [1 - (W_1/W_2)] \qquad (1)$$

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

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.

2.3.2. Electrochemical Measurements

2.3.2.1. 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 open circuit potential, E_{OCP}. All experiments

were carried out at 25 ± 1 ºC and solutions were not aerated. For polarization measurements potential from -300 to 100 mV [relative to E_{OCP}] was applied. The inhibition efficiency and surface coverage (Ө) were calculated using equation (3):

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

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

2.3.2.2. Electrochemical impedance spectroscopy (EIS) 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 extracts obtained from the impedance measurements can be calculated using equation (4):

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

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

2.3.2.3. Electrochemical frequency modulation (EFM) method

Electrochemical frequency modulation (EFM) was carried out using two frequencies 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 Tafel 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 method

The weight loss-time curves of C-steel specimens in 1 M HCl solution, with and without different concentrations from the investigated Capsicum extract, was determined after 3h of immersion at 25ºC are given in Figure 2. % IE are given in Table 1.

Table 1 - Data of weight loss measurements for C-steel in 1 M HCl solution in the absence and presence of different concentrations of Capsicum extract at temperature ranges (25-55 ºC)

Temperature, ºC	Conc., ppm	Weight loss, mg cm⁻²	Ө	% IE
	Blank	6.50	--	--
	50	1.96	0.698	69.8
	100	1.83	0.718	71.8
25	150	1.78	0.726	72.6
	200	1.58	0.757	75.7
	250	1.09	0.832	83.2
	300	0.89	0.863	86.3
	Blank	11.16	--	--
	50	3.65	0.668	66.8
	100	3.41	0.691	69.1
35	150	3.18	0.711	71.1
	200	2.99	0.727	72.7
	250	2.71	0.746	74.6
	300	2.63	0.761	76.1
	Blank	28.45	--	--
	50	10.94	0.616	61.6
	100	9.83	0.655	65.5
45	150	8.92	0.687	68.7
	200	8.28	0.709	70.9
	250	7.97	0.721	72.1
	300	7.56	0.735	73.5
	Blank	57.34	--	--
	50	25.27	0.559	55.9
	100	23.00	0.599	59.9
55	150	22.30	0.611	61.1
	200	20.50	0.642	64.2
	250	19.40	0.661	66.1
	300	18.30	0.681	68.1

The presence of Capsicum extract reduces the corrosion rate of C-steel in HCl. From the plot, weight loss for systems containing Capsicum extract was found to be lower compared to the blank indicating that different concentrations of Capsicum extract retards the corrosion of C-steel in 1 M HCl. The Figure reveals that the Capsicum extract actually inhibited the HCl induced corrosion of C-steel to an appreciable extent. The Figure also reveals that C-steel corrosion by HCl occurs not by simple homogenous process but by a heterogeneous one consisting of different or same rates. This assertion is made from the non-uniformity or nonlinearity of the plots obtained [16].
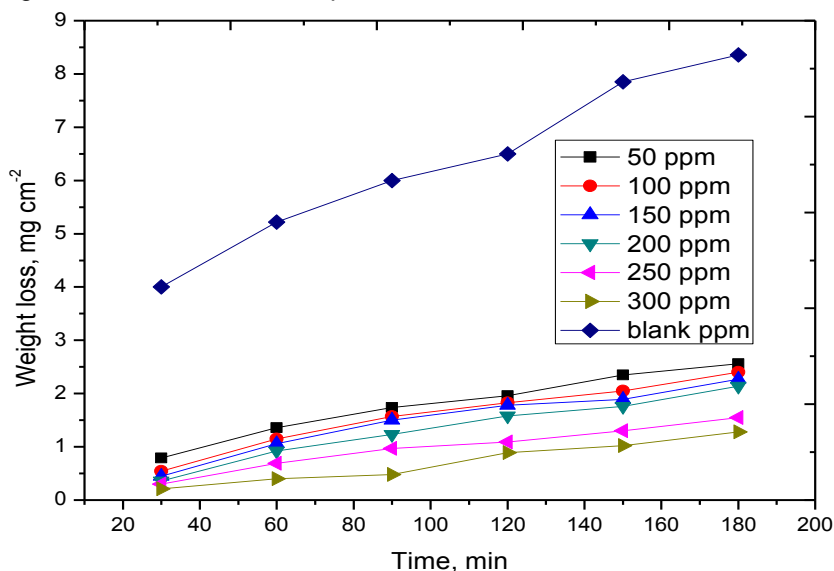

Figure 2 - Weight loss-time curves for the corrosion of C-steel in 1 M HCl in absence and presence of different concentrations of Capsicum extract at 25°C

3.2. Adsorption isotherms and thermodynamics parameters

The mechanism of the interaction between extract and the metal surface can be explained using adsorption isotherms The degree of surface coverage, θ, was computed for the different concentrations of the extract from weight loss measurements as follows: % IE = θ x 100, assuming direct relationship between surface coverage and inhibition efficiency. The surface coverage values obtained were applied to various adsorption isotherm models. By far, the best fit was found to obey Langmuir adsorption isotherm (Figure 3), which may be formulated as in equation (5):

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

where K_{ads} is the adsorption equilibrium constant of the extract and C is the extract concentration. The free energy of adsorption (ΔG°_{ads}) can be obtained from equation (6):

$$\log K_{ads} = - \log 55.5 - \Delta G^\circ_{ads}/2.303RT \qquad (6)$$

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. The negative values of ΔG°_{ads} in Table (2) suggested that the adsorption of extract 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 extract molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [17, 18]. The large K_{ads} values give better inhibition efficiency due to strong electrical interaction between the double layer and adsorbing extract molecules while a small K_{ads} values compromise that such interactions between the adsorbing extract molecules and the metal surface are weaker, indicating that the extract molecules are easily removable by the solvent molecules from the surface of C-steel. Figure (4) 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} were obtained as in Equation (7):

$$\Delta G^\circ_{ads} = \Delta H^\circ_{ads} - T\Delta S^\circ_{ads} \qquad (7)$$

The negative sign of ΔH°_{ads} indicated that the adsorption of extract molecules is an exothermic process in all cases. The sign of ΔS°_{ads} is negative because extract 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].
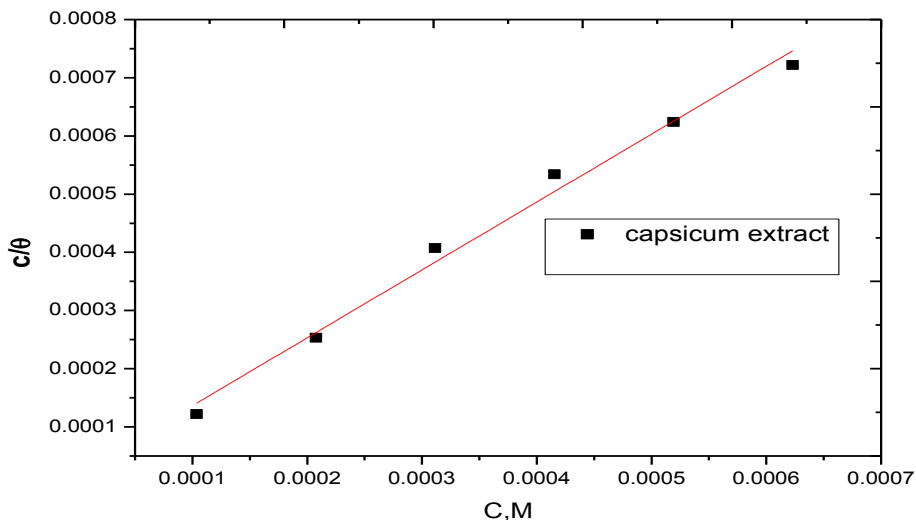
Figure 3 - Adsorption isotherm for the adsorption of extract on C-steel in 1M HCl at 25˚C

Table 2 - Thermodynamic parameters for C-steel in 1 M HCl for Capsicum extract

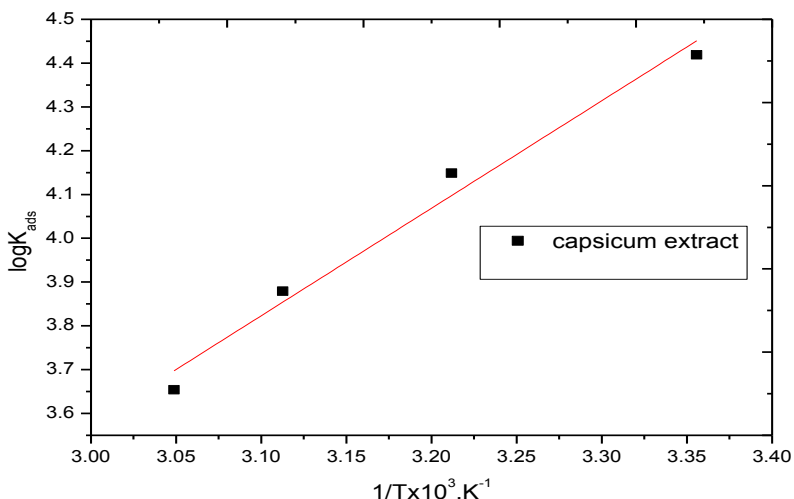| Extract	Temp., K	$-\Delta S^{\circ}_{ads}$, J mol^{-1}K^{-1}	$-\Delta H^{\circ}_{ads}$, kJ mol^{-1}	$-\Delta G^{\circ}_{ads}$, kJ mol^{-1}	$K_{ads \times 10}{}^{-3}$, M^{-1}
extract	298	37.4	46.9	35.8	50.3

Figure 4 - Variation of log K_{ads} with 1/ T

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 over-potentials increases [21]. In order to access the effect of temperature on the corrosion and corro-sion 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 (50-300 ppm) of Capsicum extract. It was found that after 3 h immersion period, the surface coverage and inhibition efficiency decrease with rise in temperature (Table 1). Arrhenius-type dependence is observed between corrosion rate and temperature often expressed as in equation (8):

Corrosion Rate (CR) =A exp - E_a^*/RT (8)

where CR is the corrosion rate, E_a^* is the apparent activation energy 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. Sati-sfactory straight lines of high correlation coeffi-cients were obtained. The values of activation ene-rgy 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 con-centrations of the extract are higher than in their absence.

Table 3 - Kinetic activation parameters for C-steel in 1M HCl in the absence and presence 150 ppm Capsicum extract

Extracts	Conc. ppm	Activation parameters		
		E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1}K^{-1}
Blank	0.0	42.0	21.0	155.3
Extract	150	74.5	55.1	97.1

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 1). 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 extract 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 ΔH^* and ΔS^* were calculated Table 3.
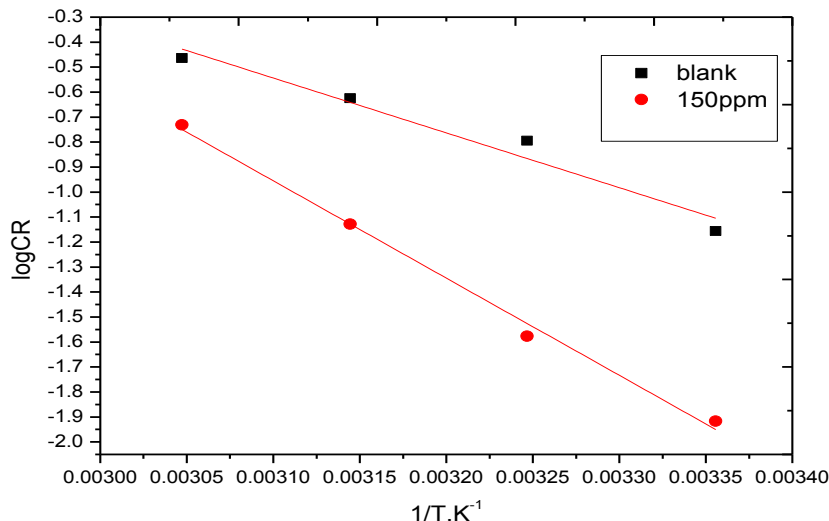

Figure 5 - Arrhenius plot of variation of (log CR) vs. 1/T) for dissolution of C-steel in 1M HCl in absence and presence of 150 ppm of Capsicum extract
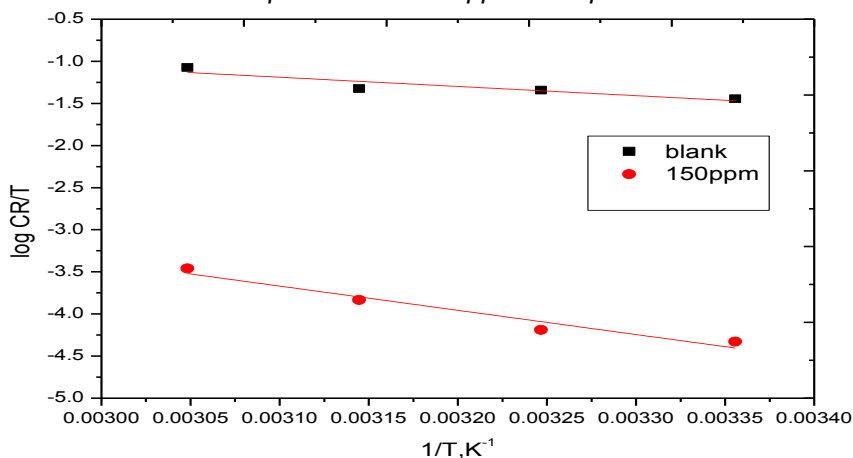

Figure 6 - Arrhenius plot of variation of (log CR/T) vs. 1/T) for dissolution of C-steel in 1M HCl in in absence and presence of 150 ppm of Capsicum extract

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. 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 Capsicum extract are shown in Figure 7. 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 Capsicum extract concentration. The decrease in corrosion current densities in the presence of extract might be due to the adsorption of Capsicum extract components molecules on the C-steel surface. In the absence and presence of Capsicum 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 extract can be seen as a cathodic or anodic type. In our study the maximum displacement was 15 mV, indicating that Capsicum extract belonged to mixed-type.

Table 4 - Corrosion parameters obtained from potentiodynamic polarization of C-steel in 1M HCl containing various concentrations of Capsicum extract at 25°C

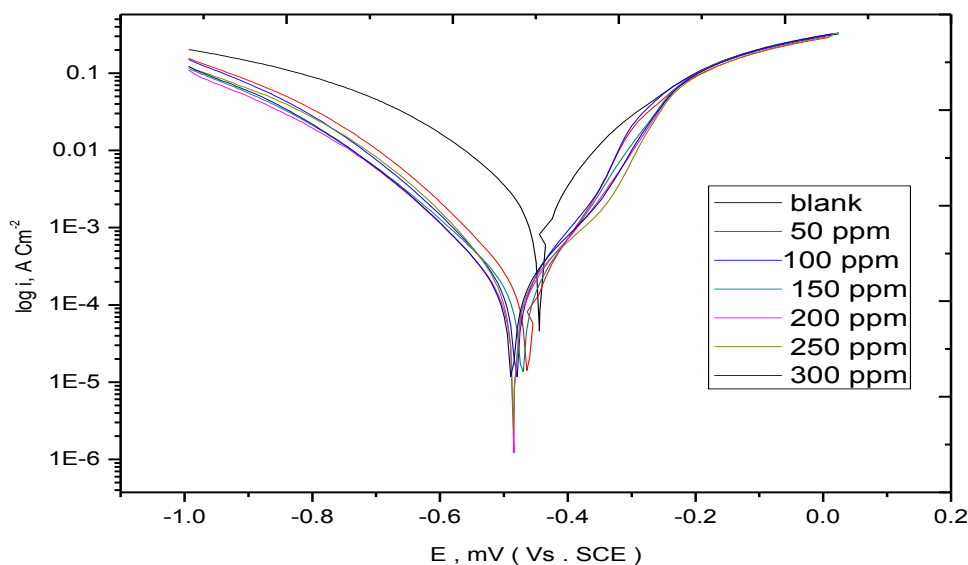| Comp.	Conc., ppm	$-E_{corr}$, mVvs.SCE	i_{corr} mA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	θ	% IE	CR mpy
Blank	0.0	449	959.0	236	160	---	---	252.9
Extract	50	462	230.4	161	97	0.760	76.0	104.9
	100	481	197.1	156	100	0.795	79.5	90.1
	150	471	190.8	172	99	0.802	80.2	86.9
	200	484	178.2	168	110	0.814	81.4	80.5
	250	485	161.60	119	138	0.832	83.2	76.9
	300	487	140.00	146	113	0.854	85.4	71.1

Figure 7 - Potentiodynamic polarization curves of C-steel in 1 M HCl in the absence and presence of different concentrations of Capsicum extract at 25°C

3.5. Electrochemical impedance spectroscopy (EIS) method

The corrosion of C-steel in 1 M HCl in the presence of Capsicum 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 (Figure 8) and are given in Table 5 for C-steel in 1M HCl acid solution in the presence and absence of the extract.
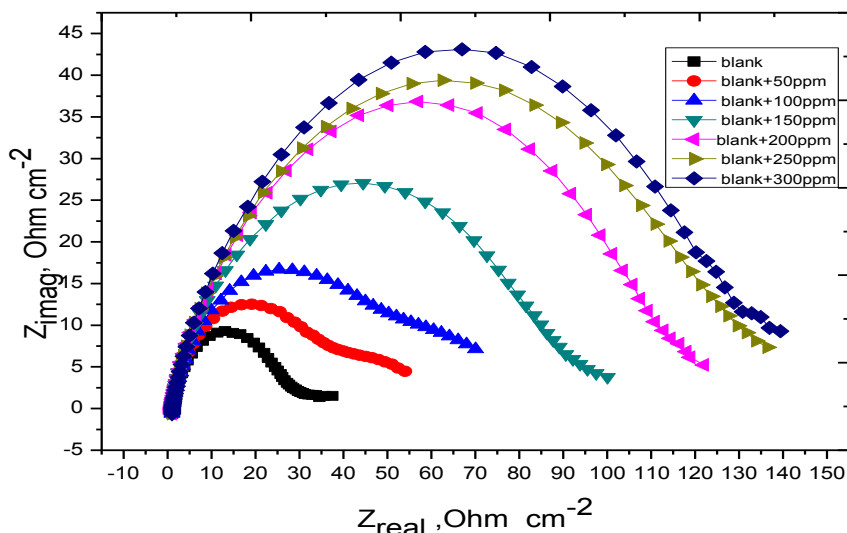

Figure 8 - Nyquist plot of C-steel in 1 M HCl in the absence and presence of different concentrations of Capsicum extract at 25°C

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 Capsicum extract. A low capacitance may result if water molecules at the electrode interface are replaced by extract molecules of lower dielectric constant through adsorption.

Table 5 - EIS data of C-steel in 1 M HCl and in the presence and absence of different concentrations of Capsicum extract at 25°C

Comp.	Conc., ppm	C_{dl}, μF cm^{-2}	n	R_{ct}, Ω cm^2	θ	% IE_{EIS}
Blank	0.0	132.0	0.834	28.5	---	---
Extract	50	110.4	0.862	41.4	0.311	31.1
	100	98.5	0.853	57.3	0.500	50.0
	150	84.1	0.814	85.5	0.667	66.7
	200	75.7	0.846	109.9	741.0	74.1
	250	70.4	0.881	125.6	0.766	76.6
	300	64.2	0.873	149.1	0.810	81.0

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 (Figure 9) 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 9:

$$C_{dl} = [1/\omega_{max} R_p] = [1/2\pi f_{max} R_p] \qquad (9)$$
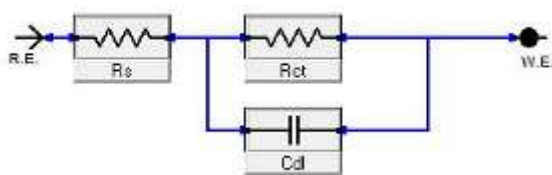
where f is maximum frequency, ω is the angular velocity

Figure 9 - Equivalent circuit model used to fit impedance data

3.6. Electrochemical frequency modulation (EFM) method

The EFM is a nondestructive 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. Intermodulation spectra obtained from EFM measurements are presented in Figures (10 and 11) as examples of C-steel in aerated 1 M HCl solutions devoid of and containing different concentrations of Capsicum extract at 25°C. Each spectrum is a current response as a function of frequency. The calculated corrosion kinetic parameters at different concentrations of Capsicum extract in 1 M HCl at 25°C (i_{corr}, β_a, β_c, CF-2, CF-3 and % IE) are given in Table (6). From Table 6, the corrosion current densities decrease by increasing the concentration of Capsicum extract and the inhibition efficiency increases by increasing the extract concentration.
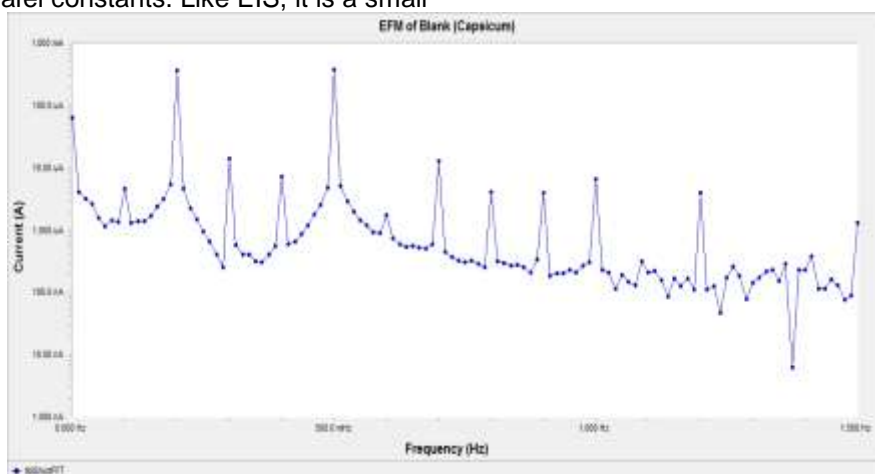

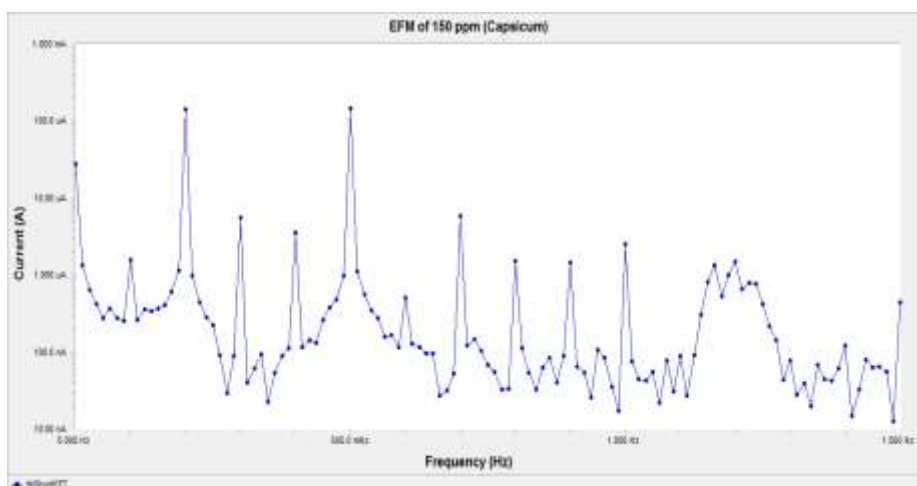*Figure 10 - EFM spectra for C-steel in 1M HCl (blank) at 25°C*

Figure 11 - EFM spectra for C-steel in 1M HCl solutions in the presence of 150 ppm Capsicum extract at 25°C

The causality factors in Table 6 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 extract is not performing very well. The obtained results showed good agreement of inhibition efficiency obtained from the potentiodynamic polarization, EIS and weight loss methods.

Table 6 - Electrochemical kinetic parameters obtained from EFM technique for C-steel in the absence and presence of various concentrations of Capsicum 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	99	1.782	2.811	----	----	287.1
Extract	50	255.5	185	140	1.643	2.641	0.593	59.3	116.8
	100	244.7	160	127	1.821	2.501	0.611	61.1	111.8
	150	238.4	135	102	1.511	2.716	0.621	62.1	108.7
	200	200.5	127	114	1.881	2.820	0.682	68.2	102.3
	250	186.1	138	124	1.943	2.900	0.704	70.4	91.6
	300	101.5	144	126	1.660	2.898	0.838	83.8	84.6

## 3.7. Energy dispersion spectroscopy (EDX) studies

The EDX 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. Figure 12 shows the EDX analysis result on the composition of C-steel only without the acid and extract treatment. The EDX analysis indicates that only Fe and oxygen were detected, which shows that the passive film contained only Fe_2O_3. Figure 12 portrays the EDX analysis of C-steel in 1M HCl only and in the presence of 300 ppm of extract. The spectra show additional lines, demonstrating the existence of C (owing to the carbon atoms of Capsicum extract). These data shows that the carbon and N materials covered the specimen surface. This layer is entirely owing to the extract, because the carbon and N signals are absent on the specimen surface exposed to uninhibited HCl. It is seen that, in addition to Mn, O, C. and N were present in the spectra. A comparable elemental distribution is shown in Table 7.

carbon steel alone
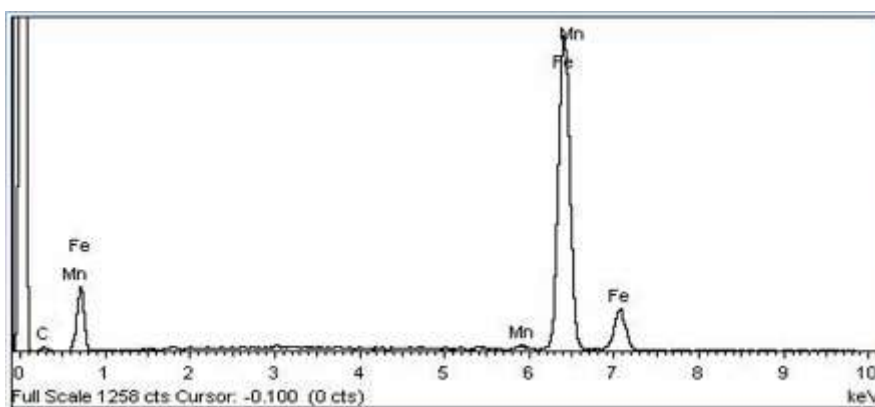
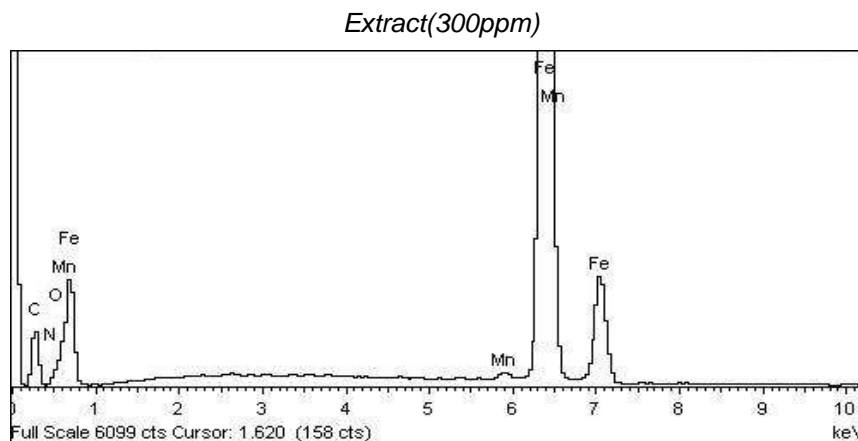*Blank*
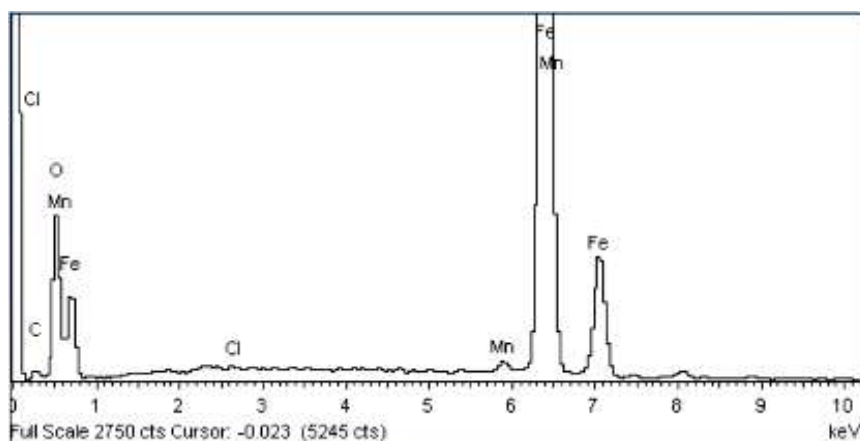
Extract(300ppm)

Figure 12 - EDX analysis on C-steel in presence and absence of 300ppm capsicum extract for 3 days immersion

Table 7 - Surface composition (weight %) of C-steel alloy after 3days of immersion in HCl without and with 300ppm of capsicum 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
Capsicum extract	60.37	0.53	20.45	12.88	6.07	----

3.8. Scanning electron microscopy (SEM) studies

Figure (13) represents the micrograph 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. Figure 13 reveals the surface on C-steel al loy after exposure to 1M HCl solution containing 300ppm of capsicum extract. It is important to stress out that when the compound is present in the solution, the morphology of C-steel alloy surfaces are 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 capsicum 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. Or due to the involvement of extract 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 [31-32].
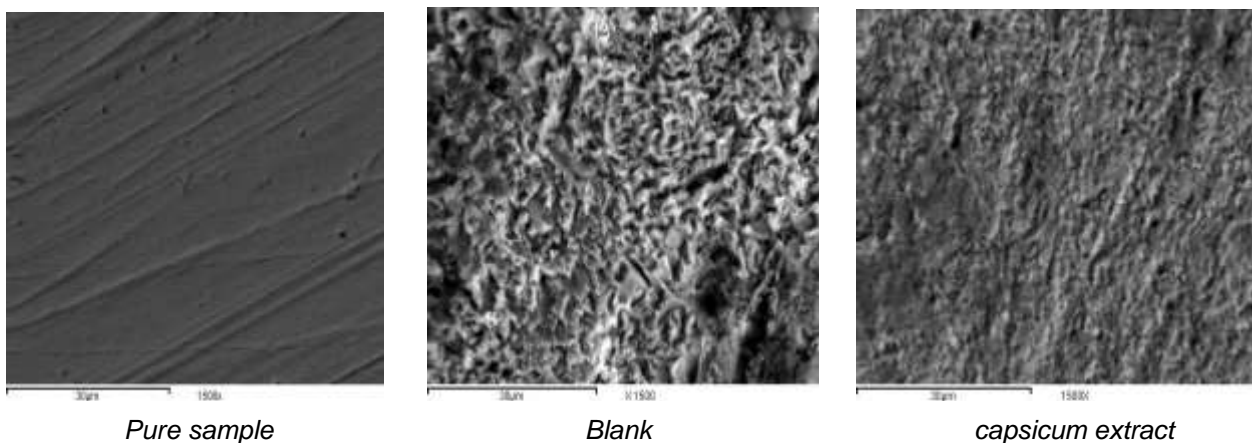

Pure sample   *Blank*   *capsicum extract*

Figure 13 - SEM micrographs for C-steel in absence and presence of 300 ppm of Capsicum extract

3.9. Mechanism of corrosion inhibition

Corrosion of C-steel in HCl was found inhibited in presence of extract. From analysis of the results obtained by various techniques it was recognized that changing surface property of steel with concentration of extract was responsible for retarded corrosion rate which corresponds to molecular adsorption of extract over C-steel surface. It is well known that most of the extracts fall under the category of adsorption type extracts 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 C-steel (electrostatic bonding) [30]. Adsorption of Cl- over C-steel surface produced unbalanced negative charge which promoted adsorption of extract molecules at most active sites and inhibition efficiency was enhanced due to synergistic effect. Also these organic compounds contain N, O heteroatoms, fused benzene rings and OH molecules in their chemical structures which contributed electrons for sharing with vacant d orbit electrons of iron (chemisorption). On the basis of facts discussed above it can be said that corrosion inhibition greatly depends upon adsorption of extract molecules over surface of C-steel. In our case adsorbed extract molecules accumulated at the metal/acid interface and constructed a layer surrounding C-steel. This layer prevented C-steel from further being corroded.

4. CONCLUSIONS

Based on the above results, the following conclusions can be drawn:

- Aqueous extract of Capsicum extract was found to be an efficient, eco-friendly and low cost extract for the corrosion of C-steel in 1 M HCl
- Inhibition efficiency increased with an increase in Capsicum extract content in 1 M HCl but decreased with rise in temperature
- The corrosion process is inhibited by adsorption of the Capsicum 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
- The negative free energy ($-\Delta G°_{ads}$) of adsorption indicates strong and spontaneous adsorption of the Capsicum extract on the C-steel surface
- Values of Tafel constants β_a and β_c confirm that the Capsicum extract acts like mixed type inhibitor
- Increase in R_{ct} values and decrease in i_{corr} and C_{dl} values confirm that the Capsicum extract is adsorbed on the C-steel surface and inhibition process is followed by monolayer adsorption
- The inhibition efficiencies determined by chemical and electrochemical methods are in reasonable good agreement
- Thus the Capsicum extract was proved to be an effective.

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IZVOD

EKSTRAKT PAPRIKE KAO ZELENI INHIBITOR ZA KOROZIJU UGLJENIČNOG ČELIKA U RASTVORU HLOROVODONIČNE KISELINE

Ekstrakt paprike je potvrđen kao zeleni inhibitor za koroziju ugljenog čelika u rastvoru 1M HCl i istraživan je preko gubitka težine, potenciodinamičke polarizacije , merenjem impedanse (EIS) , elektrohemijskog modula frekvencije (MKE), disperzne spektroskopije (EDS) i skenirajuće elektronske mikroskopije (SEM) kao metoda za praćenje korozije. Inhibitorna svojstva ekstrakta paprike se pripisuje prisustvu kapcinske i askorbinske kiseline kao glavnih sastojaka u ekstraktu. Merenja su pokazala da ovaj ekstrakt deluje kao mešoviti tip inhibitora. Efikasnost inhibicije je utvrđeno da se povećava sa povećanjem koncentracije ekstrakta. Rezultati dobijeni različitim tehnikama su blizu jedan drugom i maksimalnu efikasnost od 86% je potvrđena u koncentraciji ekstrakta od 300 ppm. Model Langmuirove izoterme je najpogodniji da bi se objasnilo adsorpcijsko ponašanje inhibitora na ugljeničnoj-čeličnoj površini. Molekularna adsorpcija ekstrakta preko ugljenične- čelične površine je proglašena krivim za inhibitorsku koroziju ugljeničnog- čelika u kiselini.

Ključne reči: *Inhibitorska korozija, ekstrakt paprike, ugljenični čelik, HCl.*