

## Aqueous Extract of Coriander Seeds as Green Corrosion Inhibitor for 304 Stainless Steel in Hydrochloric Acid Solutions

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**ABSTRACT.** Corrosion inhibition of 304 stainless steel (SS) in 1 M HCl by aqueous extract of coriander seeds was studied using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Values of inhibition efficiency obtained are dependent upon the concentration of extract and temperature. Generally, inhibition was found to increase with inhibitor concentration, but decrease with temperature. Physical adsorption mechanism has been proposed for the inhibition with Langmuir adsorption isotherm obeyed. Values of activation energy of the inhibited corrosion reaction of 304 SS are greater than the value obtained for the blank. Thermodynamic consideration reveals that adsorption of aqueous extract of coriander seeds 304 SS surface is spontaneous.

**Key words:** Corrosion, Coriander seed extract, 304 SS, Langmuir adsorption isotherm

### INTRODUCTION

Pure metals and alloys react chemically/electrochemically with corrosive medium to form a stable compound, in which the loss of metal occurs. The compound so formed is called corrosion product and metal surface becomes corroded. Corrosion involves the movement of metal ions into the solution at active areas (anode), passage of electrons from the metal to an acceptor at less active areas (cathode), an ionic current in the solution and an electronic current in the metal. The cathodic process requires the presence of an electron acceptor such as oxygen or oxidizing agents or hydrogen ions.<sup>1</sup> Corrosion of metals is a major problem that must be confronted for safety, environment, and economic reasons. It can be minimized by suitable strategies which in turn stifle, retard or completely stop the anodic or cathodic reactions or both. Among the several methods of corrosion control and prevention, the use of corrosion inhibitors, is very popular. Most of the efficient inhibitors are organic compounds that contain in their structures mostly nitrogen, sulfur or oxygen atoms. Unfortunately, the use of some chemical inhibitors has been limited because of some reasons namely their synthesis is very often expensive and they can be toxic and hazardous for human beings environment as well. This has prompted the search for eco-friendly corrosion inhibitors as an alternative to replace inorganic and organic inhibitors to foster sustainable green-

ness to the environment. These nontoxic, benign, inexpensive, renewable and readily available alternative corrosion inhibitors have been found in different parts of plant extracts.<sup>2</sup> The use of plant products as corrosion inhibitors are justified by the phytochemical compounds present therein, with molecular and electronic structures bearing close similarity to those of conventional organic inhibitor molecules.

Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. Delonix regia extracts inhibited the corrosion of aluminum in hydrochloric acid solutions,<sup>3</sup> rosemary leaves were studied as corrosion inhibitor for the Al + 2.5 Mg alloy in a 3% NaCl solution at 25 °C,<sup>4</sup> El-Etre investigated opuntia extract as corrosion inhibitor for aluminum.<sup>5</sup> The inhibitive effect of the extract of ginger on the corrosion of steel in polluted sodium chloride solution was investigated.<sup>6</sup> Also, Fouda et al.<sup>7</sup> investigated camellia sinensis as corrosion inhibitor for mild steel in chloride and aluminum sulfate solution.

The present study is aimed to investigate the inhibitive and adsorption properties of aqueous extract of coriander seeds for the corrosion of 304 SS in HCl.

### EXPERIMENTAL

#### Materials

The experiments were performed with stainless steel type

304 specimens in the form of sheets with the following composition (wt%): 18 Cr, 8 Ni, less than 0.03 C and the remainder iron. 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<sup>2</sup> to contact the test solution. Prior to each experiment, these sheets were abraded with emery paper (400–1000 grade) 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 304 SS as working electrode, platinum foil with a 1 cm<sup>2</sup> surface area as counter electrode and saturated calomel electrode (SCE) via a Luggin capillary probe was used as reference electrode. All reagents used 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.

### Aqueous Extract of Coriander Seeds

Coriander is native to regions spanning from southern Europe and North Africa to southwestern Asia. The word coriander derives from the old French coriandre, which comes from Latin coriandrum. The analysis of coriander

seeds aqueous extract showed that it contains linalool (60–80%), geraniol (1.2–4.6%), terpinen-terpinene (1–8%), caffeic acids and phenolcarboxylic acids.

### Weight Loss Measurements

The samples measuring 2×2×0.2 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 304 SS sheets could be obtained. Then the tests were carried out at a temperature range 25–45 °C. The inhibition efficiency (IE) of the inhibitor and corrosion rate (CR) in mg cm<sup>-2</sup> min<sup>-1</sup> of 304 SS in HCl solution was calculated using equations (1) and (2) respectively:<sup>8</sup>

$$\% \text{ IE} = [1 - (W_1/W_2)] \times 100 \quad (1)$$

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

where  $W_1$  and  $W_2$  are the weight losses (mg/cm<sup>2</sup>) in the presence and absence of the extract, respectively,  $A$  is the area of the specimen in cm<sup>2</sup> and  $t$  is the period of immersion in minutes.

### Potentiodynamic Polarization Measurements

Working electrode was immersed in the test solution (100 ml) for 30 min until steady state was attained this was taking as  $E_{OC}$ . 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, ( $E_{OC}$ )] was applied. The inhibition efficiency was calculated using equation<sup>7</sup> (3):

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

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

### Electrochemical Impedance Spectroscopy (EIS) Measurements

The impedance spectra were recorded at OCP after immersion of the electrode for 30 min in the test solution in order to attain steady state. The alternating current (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 ( $\theta$ ) of the used inhibitors obtained from the impedance measurements can be calculated using equation<sup>7</sup> (4):

Names & Mol. Formulas	Structures	IUPAC name & Mol. Weights
Linalool C <sub>10</sub> H <sub>18</sub> O		3,7-dimethylocta-1,6-dien-3-ol 154.25
Geraniol C <sub>10</sub> H <sub>18</sub> O		(trans)-3,7-Dimethyl-2,6-octadien-1-ol 154.25
Terpinene C <sub>10</sub> H <sub>16</sub>		β:4-methylene-1-(1-methylethyl)cyclohexene 136.23
Caffeic acid C <sub>9</sub> H <sub>8</sub> O <sub>4</sub>		3,4-Dihydroxycinnamic acid 180.16
phenolcarboxylic acids	Mono, di and tri-hydroxybenzoic acid	

**Figure 1.** Molecular structures, names, molecular weights and molecular formulas of main components in aqueous extract of coriander seeds.

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

$R_{ct}^{\circ}$  and  $R_{ct}$  are the charge transfer resistance in the absence and presence of inhibitor, respectively.

### Electrochemical Frequency Modulation (EFM) Measurements

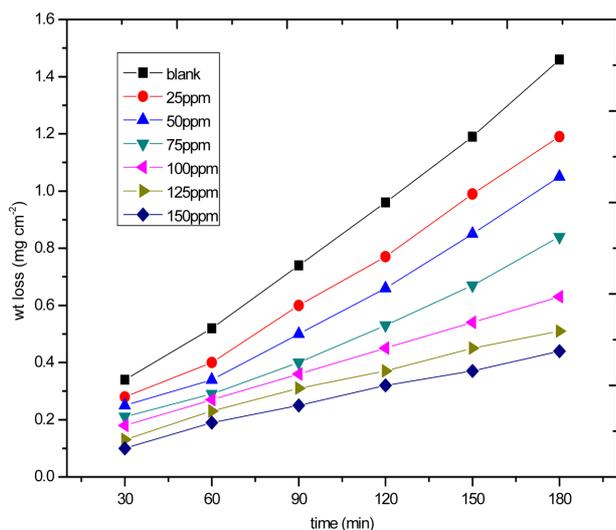
Electrochemical frequency modulation was carried out using two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1s. The Intermodulation spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density ( $i_{\text{corr}}$ ), the Tafel slopes ( $\beta_c$  and  $\beta_a$ ) and the causality factors CF-2 & CF-3.<sup>9,10</sup>

All electrochemical experiments were carried out using Potentiostat/Galvanostat/Zra analyzer (Gamry PCI300/4, USA). 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 tting and calculating.

## RESULTS AND DISCUSSION

### Weight Loss Measurements

The weight loss-time curves of 304 SS specimens in 1 M HCl solution, with and without different concentrations of the investigated coriander seeds extract, were determined after 3 h of immersion at 25 °C and are given in Fig. 2. % IE are given in Table 1. The presence of extract reduces the



**Figure 2.** Weight loss-time curves for the corrosion of 304 SS in 1 M HCl in absence and presence of different concentrations of coriander extract at 25 °C.

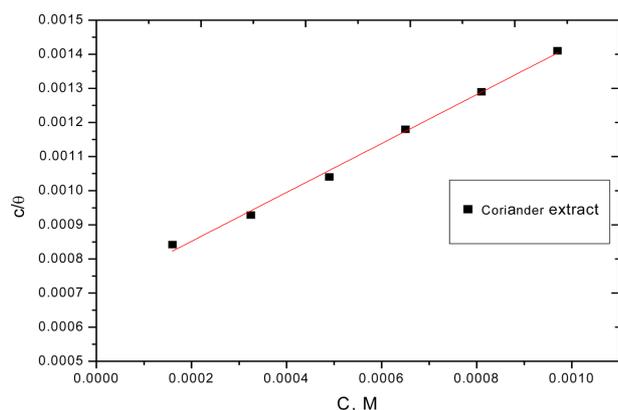
**Table 1.** Data of weight loss measurements for 304 SS in 1 M HCl solution in the absence and presence of different concentrations of coriander extract at temperature ranges (25–40 °C)

Temp. °C	Conc., ppm	Weight loss, mg cm <sup>-2</sup>	$\theta$	% IE
25	25	0.749	0.401	41.1
	50	0.660	0.472	47.2
	75	0.521	0.583	58.3
	100	0.485	0.621	62.1
	125	0.378	0.689	68.9
	150	0.316	0.747	74.7
30	25	0.890	0.341	34.1
	50	0.790	0.415	41.5
	75	0.680	0.496	49.6
	100	0.550	0.593	59.3
	125	0.480	0.644	64.4
	150	0.410	0.696	69.6
35	25	0.890	0.341	34.1
	50	0.790	0.415	41.5
	75	0.680	0.496	49.6
	100	0.570	0.578	57.8
	125	0.480	0.644	64.4
	150	0.430	0.681	68.1
40	25	1.050	0.300	30.0
	50	0.930	0.380	38.0
	75	0.840	0.440	44.0
	100	0.730	0.513	51.3
	125	0.570	0.620	62.0
	150	0.600	0.600	62.7

corrosion rate of 304 SS in HCl. From the plot, weight loss for systems containing coriander extract was found to be lower compared to the blank, indicating that different concentrations of coriander extract retard the corrosion of 304 SS in 1 M HCl. The Figure reveals that the plant extract actually inhibited the HCl induced corrosion of 304 SS to an appreciable extent. The Figure also reveals that 304 SS 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.<sup>11</sup>

### Adsorption Isotherm and Thermodynamic Parameters

The mechanism of the interaction between inhibitor and the metal surface can be explained using adsorption isotherms. The degree of surface coverage,  $\theta$ , was computed for the different concentrations of the extract from weight loss measurements as follows: % IE =  $\theta \times 100$ , assuming direct relationship between surface coverage and inhibition efficiency. The surface coverage values obtained were applied to



**Figure 3.** Adsorption isotherm for the adsorption of extract on 304 SS in 1 M HCl at 25 °C.

various adsorption isotherm models. By far, the best fit was found to obey Langmuir adsorption isotherm (Fig. 3), which may be formulated as in equation<sup>9</sup> (5):

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

where  $K_{\text{ads}}$  is the adsorption equilibrium constant of the inhibitor,  $C$  is the inhibitor concentration and  $\theta$  is the surface coverage. The free energy of adsorption ( $\Delta G_{\text{ads}}^{\circ}$ ) can be obtained from equation<sup>9</sup> (6):

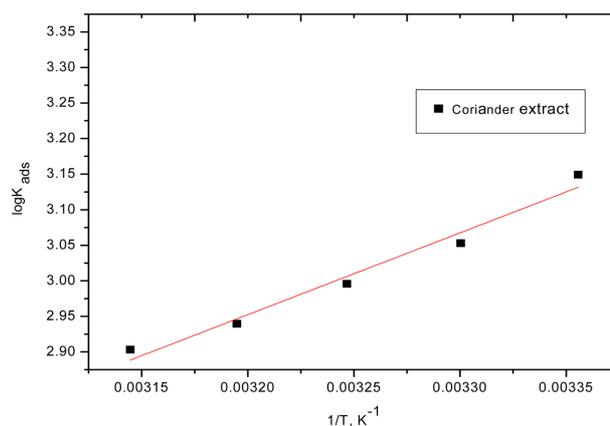
$$\log K_{\text{ads}} = -\log 55.5 - \Delta G_{\text{ads}}^{\circ}/2.303RT \quad (6)$$

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.

The negative values of  $\Delta G_{\text{ads}}^{\circ}$  in Table 2 suggested that the adsorption of inhibitor molecules onto 304 SS surface is a spontaneous process. Generally, values of  $\Delta G_{\text{ads}}^{\circ}$  up to  $-20 \text{ kJ mol}^{-1}$  are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than  $40 \text{ kJ mol}^{-1}$  involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption).<sup>12,13</sup> The large  $K_{\text{ads}}$  value gives better inhibition efficiency due to strong electrical interaction between the double layer and adsorbing inhibitor molecules while a small  $K_{\text{ads}}$  value compromise that such interactions between the adsorbing inhibitor molecules and the metal surface are weaker, indicating that the

**Table 2.** Thermodynamic parameters for 304 SS in 1 M HCl for coriander seeds extract

Inhibitor	Temp., K	$-\Delta S_{\text{ads}}^{\circ}$ $\text{J mol}^{-1}\text{K}^{-1}$	$-\Delta H_{\text{ads}}^{\circ}$ $\text{kJ mol}^{-1}$	$-\Delta G_{\text{ads}}^{\circ}$ $\text{kJ mol}^{-1}$	$K_{\text{ads}}$ $\text{M}^{-1}$
Extract	298	19.5	22.1	27.9	1410



**Figure 4.** Variation of  $\log K_{\text{ads}}$  with  $1/T$ .

inhibitor molecules are easily removable by the solvent molecules from the surface of 304 SS. Fig. 4 shows the plot of  $\log K_{\text{ads}}$  vs  $1/T$ , a straight line with an intercept equal to  $\Delta H_{\text{ads}}^{\circ}$  and with slope equal to  $\Delta S_{\text{ads}}^{\circ}$  in Equation (7):

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads}}^{\circ} - T\Delta S_{\text{ads}}^{\circ} \quad (7)$$

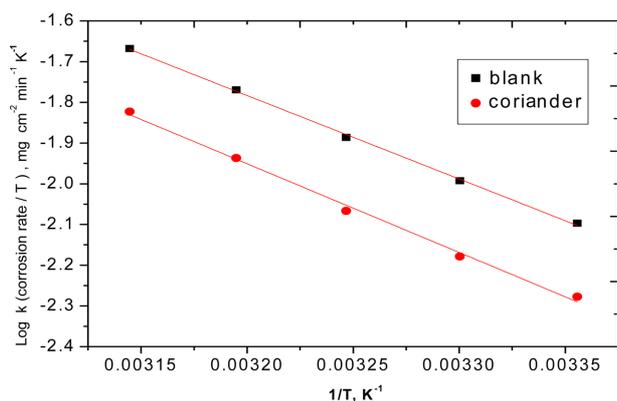
The negative sign of  $\Delta H_{\text{ads}}^{\circ}$  indicated that the adsorption of inhibitor molecules is an exothermic process in all cases. The sign of  $\Delta S_{\text{ads}}^{\circ}$  is negative because inhibitor molecules freely moving in the bulk solution were adsorbed in an orderly fashion on to 304 SS, resulting in a decrease in entropy.<sup>14</sup> Moreover, from thermodynamic principles, since the adsorption was an exothermic process, it must be accompanied by a decrease in entropy.<sup>15</sup>

### 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.<sup>16</sup> 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 of 25–40 °C in 1 M HCl in the absence and presence of different concentrations (25–150 ppm) of coriander seeds 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<sup>20</sup> 8:

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

where  $k$  is the corrosion rate constant and  $E_a^*$  is the apparent activation energy, and  $A$  is the frequency factor. Fig. 5 depicts an Arrhenius plot (logarithm of  $k$  against the recip-



**Figure 5.** Arrhenius plot of variation of ( $\log k$ ) vs ( $1/T$ ) for dissolution of 304 SS in 1M HCl in the absence and presence of 50 ppm of coriander extract.

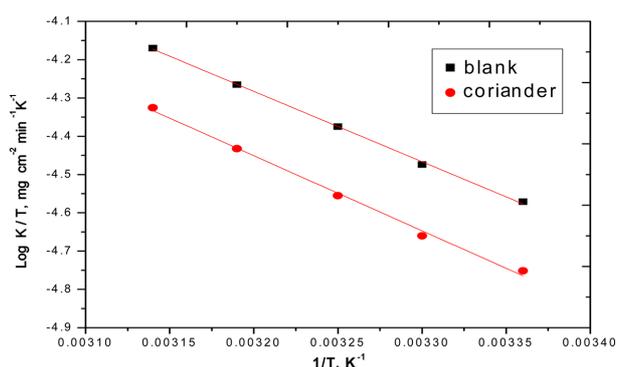
**Table 3.** Kinetic activation parameters for 304 SS in 1 M HCl in the absence and presence of 50 ppm coriander seeds extract

Inhibitors	Conc. ppm	Activation parameters		
		$E_a^*$ , kJ mol <sup>-1</sup>	$\Delta H^*$ , kJ mol <sup>-1</sup>	$-\Delta S^*$ , J mol <sup>-1</sup> K <sup>-1</sup>
Blank	0.0	39.2	36.7	162.1
Extract	50	41.7	38.5	158.2

rocal of temperature ( $1/T$ ) for 304 SS 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 from Table 3 that  $E_a^*$  values in the presence of the different concentrations of the extract are higher than in their absence. This denotes that the adsorption is physically while the reverse is usually attributed to chemical adsorption.<sup>17</sup> This conclusion is denoted by the decrease in inhibition efficiency with increasing temperature (Table 1). Similar result has been reported by Okafor et al.<sup>18</sup> 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.<sup>19</sup> An alternative formulation of Arrhenius equation is:<sup>20</sup>

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

where  $h$  is the Planck's constant,  $N$  is the Avogadro's number,  $\Delta S^*$  is the entropy of activation, and  $\Delta H^*$  is the enthalpy of activation. Fig. 6 shows a plot of  $\log (k/T)$  as a function of  $1/T$ . Straight lines were obtained with a slope of  $(\Delta H^*/R)$  and an intercept of  $(\ln R/Nh - \Delta S^*/R)$  from which the values of  $\Delta H^*$  and  $\Delta S^*$  were calculated Table 3. The positive values of  $\Delta H^*$  both in the absence and pres-

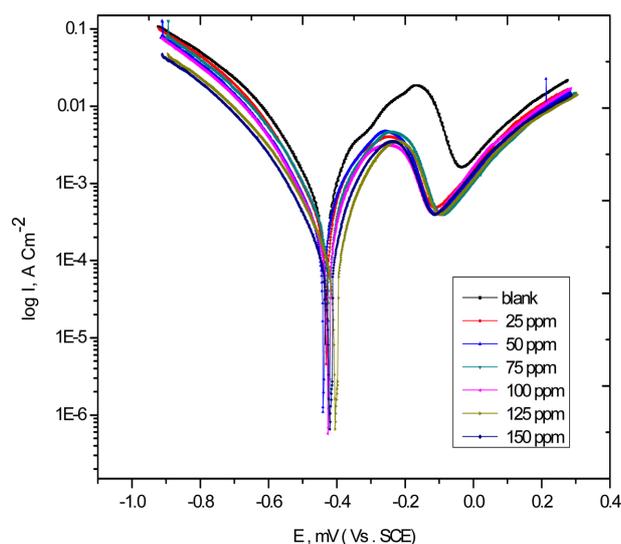


**Figure 6.** Arrhenius plot of variation of ( $\log k/T$ ) vs. ( $1/T$ ) for dissolution of 304 SS in 1 M HCl in the absence and presence of 50 ppm of coriander extract.

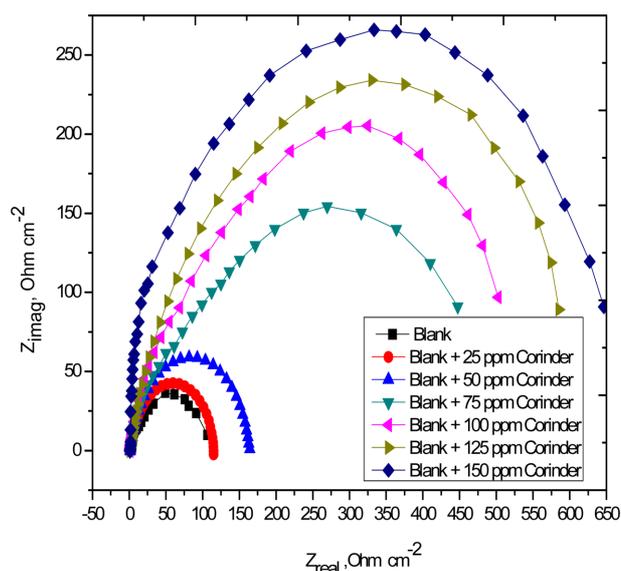
ence of the extract reflect the endothermic nature of the 304 SS dissolution process. It is also clear that the activation enthalpies vary in the same manner as the activation energies, supporting the proposed inhibition mechanism. Large and negative values of entropies imply that the activated complex 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.<sup>21</sup>

### Potentiodynamic Polarization Measurements

Potentiodynamic polarization curves for 304 SS in uninhibited and inhibited acidic solutions containing different concentrations of coriander seeds extract are shown in Fig. 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 304 SS in 1 M HCl solution decreased with increase in coriander seeds extract concentration. The decrease in corrosion current densities in the presence of the extract might be due to the adsorption of coriander seeds extract components molecules on the 304 SS surface. In the absence and presence of coriander seeds extract,  $\beta_a$  and  $\beta_c$  values remain almost constant indicating that the presence of extract not changes 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<sup>22</sup> 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, indi-



**Figure 7.** Potentiodynamic polarization curves of 304 SS in 1 M HCl in the absence and presence of different concentrations of coriander seeds extract at 25 °C.



**Figure 8.** Nyquist plot of 304 SS in 1 M HCl in the absence and presence of different concentrations of coriander seeds extract at 25 °C.

cating that coriander seeds extract belonged to mixed-type.

### Electrochemical Impedance Spectroscopy (EIS)

The corrosion of 304 SS in 1 M HCl in the presence of coriander seeds extract was investigated by EIS method at 25 °C. 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. 8)

and are given in Table 5 for 304 SS 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 304 SS in 1 M HCl acid solution. Impedance diagram have a semicircular appearance; the diagram indicates that the corrosion of 304 SS is mainly controlled by a charge transfer process.<sup>23</sup> The values of double layer

**Table 4.** Corrosion parameters obtained from potentiodynamic polarization of 304 SS in 1 M HCl containing various concentrations of coriander seeds extract at 25 °C

Comp.	Conc., ppm	$-E_{corr}$ , mV vs SCE	$i_{corr}$ , mA cm <sup>-2</sup>	$\beta_c$ , mV dec <sup>-1</sup>	$\beta_a$ , mV dec <sup>-1</sup>	$\theta$	% IE	C.R., mm y <sup>-1</sup>
Blank	0.0	444	493.0	215.0	195.3	–	–	5.022
	25	431	269.2	221	190.3	0.454	4.45	2.740
Extract	50	440	213.0	209	187.1	0.568	56.8	2.169
	75	430	172.1	206	184.3	0.651	65.1	1.753
	100	428	145.9	198	181.4	0.704	70.4	1.488
	125	425	110.9	210	178.3	0.775	77.5	1.129
	150	421	92.2	203	175.4	0.813	81.3	0.939

**Table 5.** EIS data of 304 SS in 1 M HCl and in the presence and absence of different concentrations of coriander extract at 25 °C

Comp.	Conc., ppm	$R_s$ , $\Omega$ cm <sup>2</sup>	$C_{dl}$ , $\mu$ F cm <sup>2</sup>	$n$	$R_{ct}$ , $\Omega$ cm <sup>2</sup>	$\theta$	% IE <sub>EIS</sub>
Blank	0.0	1.321	30.597	0.834	89.2	–	–
	25	1.231	24.245	0.881	120.3	0.258	25.8
Extract	50	1.161	21.234	0.872	168.1	0.470	47.0
	75	1.148	18.922	0.842	430.2	0.793	79.3
	100	1.120	16.943	0.836	500.6	0.822	82.2
	125	1.112	15.321	0.871	575.2	0.845	84.5
	150	1.108	13.521	0.869	650.9	0.863	86.3

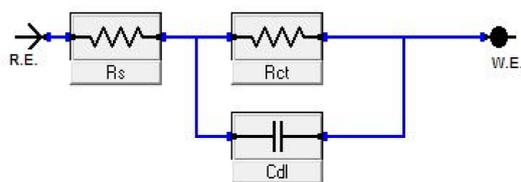


Figure 9. Equivalent circuit model used to fit impedance data.

capacitance,  $C_{dl}$ , decrease with increasing the concentration of coriander seeds extract. A low capacitance may result if water molecules at the electrode interface are replaced by inhibitor molecules of lower dielectric constant through adsorption. When such low capacitance values are connected with high  $R_{ct}$  values, it is apparent that a relationship exists between adsorption and inhibition.

The impedance data of 304 SS in 1 M HCl are analyzed in terms of an equivalent circuit model (Fig. 9) which includes the solution resistance  $R_s$  and the double layer capacitance  $C_{dl}$  which is placed in parallel to the charge transfer resistance  $R_{ct}$  due to the charge transfer reaction.  $C_{dl}$  can be calculated from the angular frequency ( $\omega_{max} = 2\pi f$ ) at the maximum imaginary component and the charge transfer resistance according equation<sup>9</sup> (10):

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

where  $f_{max}$  is maximum frequency,  $\omega$  is the angular velocity.

### Electrochemical Frequency Modulation (EFM) Measurements

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 Figs. 10 and 11 as examples of 304 SS in aerated 1 M HCl solutions devoid of and containing 150 ppm of coriander extract at 25 °C. Each spectrum is a current response as a function of frequency. The calculated corrosion kinetic parameters at

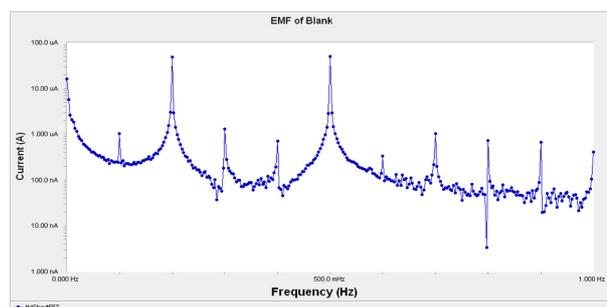


Figure 10. EFM spectra for 304 SS in 1M HCl (blank) at 25 °C.

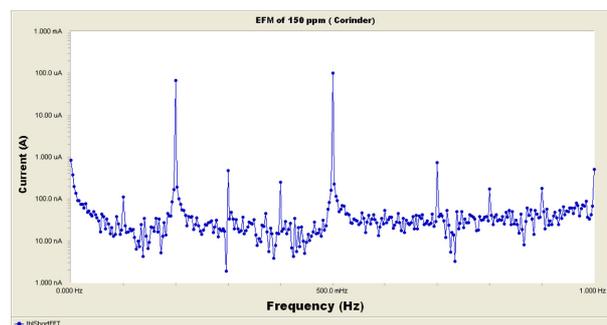


Figure 11. EFM spectra for 304 SS in 1M HCl solution in the presence of 150 ppm coriander seeds extract at 25 °C.

different concentrations of coriander extract in 1 M HCl at 25 °C ( $i_{corr}$ ,  $\beta_a$ ,  $\beta_c$ , CF-2, CF-3 and % IE) are given in Table 6. From Table 6, the corrosion current densities decrease by increasing the concentration of coriander extract and the inhibition efficiency increases by increasing the extract concentration. 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 (2 & 3) might be due to the small values of perturbation amplitude or due to the resolution of the frequency spectrum is not high enough. Another possible explanation, the inhibitor is not performing very well. The

Table 6. Electrochemical kinetic parameters obtained from EFM technique for 304 SS in the absence and presence of various concentrations of coriander seeds extract in 1 M HCl at 25 °C

Comp.	Conc., ppm	$i_{corr}$ , $\mu A cm^{-2}$	$\beta_c$ , $mV dec^{-1}$	$\beta_a$ , $mV dec^{-1}$	CF-2	CF-3	$\theta$	% IE	CR, $mm y^{-1}$
Blank	00	5330.5	233	212	1.78	2.811	–	–	7.216
	25	2776.7	220	205	1.65	2.78	0.479	47.9	3.759
Extract	50	2461.4	212	201	1.76	2.89	0.538	53.8	3.332
	75	2200.6	201	194	1.92	2.67	0.587	58.7	2.979
	100	1710.1	194	180	1.82	2.59	0.679	67.9	2.315
	125	1280.2	188	173	1.89	2.92	0.760	76.0	1.733
	150	800.8	181	162	1.69	2.88	0.850	85.0	1.084

obtained results showed good agreement of inhibition efficiency obtained from the potentiodynamic polarization, EIS and weight loss methods.

### Mechanism of Corrosion Inhibition

By examining the chemical composition of coriander extract, Table 1 shows that the aqueous extracts of coriander contain linalool (60–80%), geraniol (1.2–4.6%), terpinen-terpinene (1–8%), caffeic acid, phenol carboxylic acids (mono-, di-, and tri-hydroxybenzoic acids). In view of these components it is clear that the majority of organic compounds contain oxygen, and all have pairs of free electrons, so these compounds will be able to adsorb on 304 SS surface through the free electrons on the oxygen atoms. The occurrence of the adsorption of the compounds in the extracts on 304 SS surface constitutes the barrier for mass and charge transfer, leading to reduced interaction between the sample with central corrosion and thus decrease the corrosion rate, moreover, these compounds may be form complexes with ions of iron, causing the covering (lock) of anodic sites (microanodes) and/or cathodic sites (microcathodes) generated on the 304 SS surface under conditions of corrosion and lead to disability soluble of iron.

It is interesting to note that a number of the above named organic compounds exhibit antioxidant activity. For example, caffeic acids (phenolic compounds) are antioxidants.<sup>24</sup> Results of earlier studies suggest that antioxidant compounds in plant extracts contribute to inhibition of steel corrosion in some acidic medium.<sup>25,26,2</sup>

### CONCLUSIONS

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

(1) Coriander seeds extract was found to be an effective eco friendly and low cost inhibitor.

(2) Inhibition efficiency increased with an increase in coriander seeds extract in 1 M HCl but decreased with rise in temperature.

(3) Coriander seeds extract adsorbed physically on 304 SS surface following the Langmuir adsorption isotherm.

(4) Values of Tafel constants  $\beta_a$  and  $\beta_c$  confirm that the coriander seeds extract acts like mixed type inhibitor.

(5) The inhibition efficiencies determined by weight loss and electrochemical methods are in reasonable good agreement.

(6) Thus the coriander seeds extract was proved to be good inhibitor.

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