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Corrosion inhibition of steel by Coriander extracts in hydrochloric acid solution

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Abstract
Corrosion inhibition of steel using an aqueous extracts of Coriander (*Coriander sativum*) and some natural additives (Paprika, Clove, Cinnamon, Black piper and Pomegranate husk) in 0.5 M HCl was investigated using electrochemical polarization and EIS methods. The results indicate that the corrosion inhibition efficiency increases with an increasing Coriander extract concentration, when Coriander extract concentration exceeds 900 ppm the inhibition efficiency decreases. The addition of 87.5 ppm of some additives to a solution containing 0.5 M HCl and 300 ppm of Coriander extract enhanced the corrosion inhibition process in the following order:

Paprika > Clove>Cinnamon > Black piper > Pomegranate husk

The effect of temperature on the corrosion behavior of steel indicates that inhibition efficiency of the Coriander extract decreases with the rise of temperature. The adsorption isotherm of Coriander extracts on the steel has been determined and found to follow langmuir adsorption isotherm where the negative value of free energy of adsorption indicates that the adsorption of the Coriander extracts on the steel surface occurs spontaneously.

Keywords: Coriander; inhibition; corrosion, steel, EIS, polarization.

1. Introduction
Inhibitors are quietly required to protect metals and alloys against acid attack by reducing the corrosion rate of metals and alloys. Steel is considered to be one of the most important metals, which is frequently used in different industrial applications. The inhibition of steel corrosion in various media using large number of either synthesized [1-6] or extracted from aromatic herbs, spices and medical plant [7-13] was studied. Organic compounds, especially those containing nitrogen, sulfur and oxygen as well as heterocyclic compounds containing polar groups and π electrons gave a good inhibition by creating a barrier to corroding attack via adsorption on the surfaces. The adsorption bond strength is dependent on the composition of the metal, the inhibitor structure and concentration as well as temperature.

This work describes the inhibition effect of the aqueous extract of Coriander (*Coriander sativum*) on the corrosion of steel in HCl (0.5 M) solution in absence and presence of some additives such as (Pomegranate husk, Black piper, Cinnamon, Clove and Paprika).

2. Experimental
Steel samples of composition (wt%): C 0.2%, Mn 0.6%, P 0.04%, Si 0.003% and Fe 99.157% have been used as working electrode. The metal specimens were polished with successive grades of emery papers (600 and 1200), degreased with acetone and then rinsed with running distilled water before it immersed in the test solution. The aggressive solution (0.5 M HCl) is prepared by dilution of analytical grade 37% HCl with distilled water. The stock solution of inhibitor is prepared by Soaking 3.0 g of the inhibitor(Coriander) in 20 ml of distilled water at 60˚C for 24 hr, blending the mixture followed by filtration. Different amounts of the filtrate were added to the corrosive solution to get different concentrations 300, 600, 900, 1200 and 1500 ppm of the Coriander. The stock solution of each additive (cinnamon, black piper, clove, pomegranate husk and paprika) is prepared by soaking 0.25 g of the additive in 20 ml of 1.0 M HCl at 60˚C for 24 hr followed by filtration where the filtrate was used to prepare a solution containing 87.5 ppm of additive, 300 ppm of Coriander and 0.5 M HCl.

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Electrochemical measurements are carried out in a conventional three-electrode glass cell. The working electrode was in the form of a disc cut from steel and has a geometric area of 1 cm^2. Saturated calomel electrode (SCE) and a sheet of platinum electrode of area 2 cm^2 are used as reference and auxiliary electrodes, respectively. The polarization curves are recorded using a potentiostat (ACM instrument – Gill AC), at a scan rate of 200 mV min^{-1} in the range from -800 mV to 400 mV . The immersion time before each measurement was 180 min. to access an equilibrium potential. The impedance measurements were carried out in the frequency range of (0.01-30) Hz at the open circuit potential (OCP).

3. Results and Discussion

3-1 Polarization measurements:

Potentiodynamic polarization curves for the steel in 0.5 M HCl containing different concentrations of Coriander extracts are represented in Fig.1. Electrochemical corrosion parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c , b_a) and corrosion current density (I_{corr}), obtained by extrapolation of Tafel lines, are given in Table (1). The inhibition efficiency %IE was calculated using the following equation [14]:

$$\%IE = \frac{I^o_{corr} - I_{corr}}{I^o_{corr}} x100 \ldots\ldots\ldots\ldots(1)$$

Where I^o_{corr} and I_{corr} are the corrosion current densities in absence and presence of Coriander extract respectively. It seems that the addition of Coriander extracts shifted the corrosion potential E_{corr} to less negative potential, lowered current density (corrosion rate) and increased the inhibition efficiency %IE, This behavior reflects the Coriander extract acts as corrosion inhibitor which may be related to the adsorption of the Coriander extract molecules at the active sites of the electrode surface. On the other hand, the numerical values of both anodic and cathodic Tafel constants are decreased as the concentration of extract was increased, which indicate decreasing of both the anodic dissolution of steel and the hydrogen evolution reaction. These results indicate that the inhibitor under investigation acts as a mixed type inhibitor [15].

These results confirm that Coriander acts as an efficient corrosion inhibitor and its inhibition efficiency was increased as its concentration was increased up to 900 ppm, where maximum inhibition efficiency (78.76%) was obtained at a concentration of 900 ppm. When the concentration of Coriander extract exceeds 900 ppm, the inhibition efficiency starts to decrease. So it is concluded that the hydrogen evolution reaction is catalyzed at concentrations > 900 ppm from Coriander compounds.

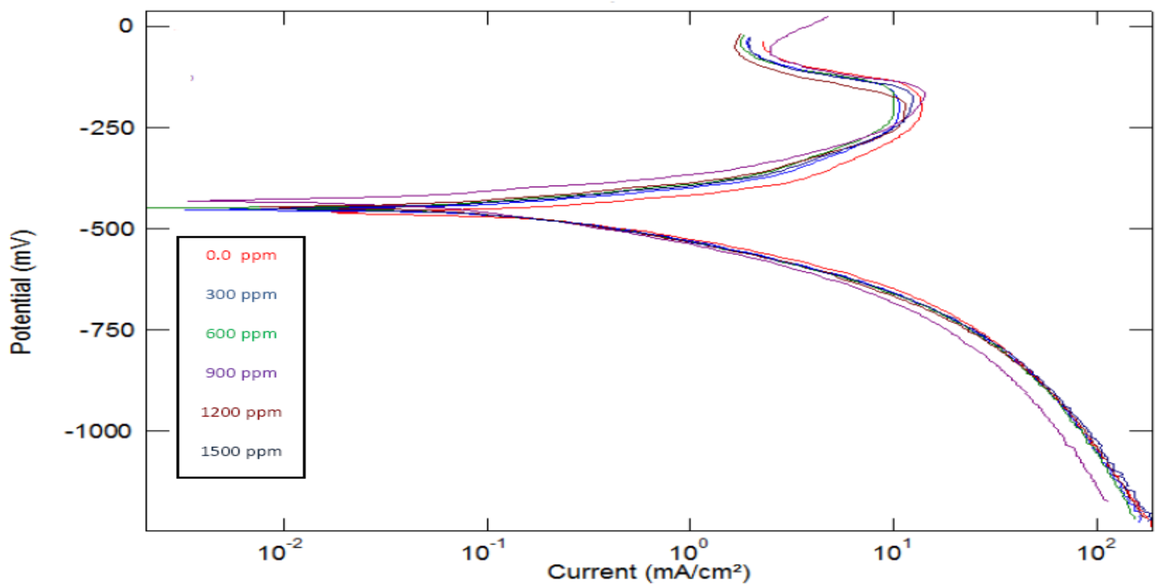

Fig. 1. Polarization curves for steel in 0.5 M HCl at different concentrations of Coriander extracts at 20 ˚C.

Polarization profiles for steel in 0.5 M HCl containing 300 ppm of Coriander extract and 87.5 ppm of different natural additives at 20˚C are shown in Fig. 2. The electrochemical corrosion parameters are given in Table 2. It seems that the addition 87.5 ppm of different natural additives inhibited the corrosion processes where it affected the anodic part of the polarization curves by different degrees as an indication that their inhibitive effect depends vary with the type of natural additives. The maximum inhibition efficiency (72.60%) was obtained on the addition of Paprika. From the polarization curves it was noted that the current density was decreased in the following order:

Pomegranate husk> Black piper> Cinnamon> Clove> Paprika

Table (1) Electrochemical corrosion parameters for steel in 0.5 M HCl containing different concentrations of Coriander extracts at 20˚C.

C (ppm)	E_{corr} (mv)	I_{corr}(mA\cm^2)	b_c (mV)	b_a(mV)	% IE
0	-457.33	1.46	228.19	202.94	-
300	-451.67	1.26	227.89	218.25	13.69
600	-448.11	0.75	191.9	173.8	48.63
900	-431.84	0.31	162.73	108.93	78.76
1200	-444.48	0.82	205.57	170.14	43.83
1500	-448.45	1.3	223.79	223.4	10.95

The inhibition efficiency data showed that the Paprika molecules have greater interaction with steel compared to other additives as the following order:

Paprika > Clove>Cinnamon > Black piper > Pomegranate husk

The order reflects the important role played by the molecular size and the substituent group of additive molecules as well as the type of the functional adsorption atom in the inhibition processes. It is clear from table 2 that Tafel slope in the anodic region, b_a, was decreased on the addition of 87.5 ppm of an additive to a solution containing 0.5 M HCl and 300 ppm of Coriander extract and it is vary with the type of the additive where the lowest value was obtained for paprika. This behavior may be ascribed to an increase in the transference coefficient as an indication of inhibition of electron transfer in the anodic region. Consequently, the addition of an additive blocks the active sites that are still not blocked by Coriander and works as co-inhibitor with Coriander extract that aid to increases the degree of corrosion inhibition efficiency. It seems that the addition of paprika, black piper and Clove works together with Coriander as mixed inhibitors that inhibit both the anodic and cathodic processes.

Table (2) Electrochemical corrosion parameters for steel in 0.5 M HCl containing 300 ppm of Coriander extract and 87.5 ppm of different additives at 20˚C.

Additives+ coriander in HCl(0.5M)	E_{corr} (mV)	I_{corr} (mA\cm^2)	b_c (mV)	b_a (mV)	% IE
0	-457.33	1.46	228.19	202.94	-
Paprika + coriander	-431.37	0.4	186.09	121.29	72.60
Clove+ coriander	-436.93	0.8	205.38	156.21	45.21
cinnamon+ coriander	-444.64	0.99	245.94	187.52	32.19
black piper+ coriander	-445.83	1.04	197.13	167.12	28.77
pomegranate husk+	-446.26	1.29	264.02	197.78	11.64

3-2 *Electrochemical impedance measurements:*

The Nyquist plots for steel in 0.5 M containing various concentrations of aqueous extracts of Coriander are shown in Fig. 3 . It is clear from the plots that the impedance response of steel in the attack solution was changed after the addition of the Coriander extracts .Table 3 collects various parameters such as charge-transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and inhibition efficiency percentage (%IE) calculated from the following equation [14]:

$$IE\% = \frac{R_{ct(inh)} - R_{ct(acid)}}{R_{ct(inh)}} \times 100 \qquad (2)$$

Where $R_{ct\ (inh)}$ and $R_{ct\ (acid)}$ are the charge-transfer resistance values in the presence and absence of Coriander extract, respectively, and are inversely proportional to corrosion rate.

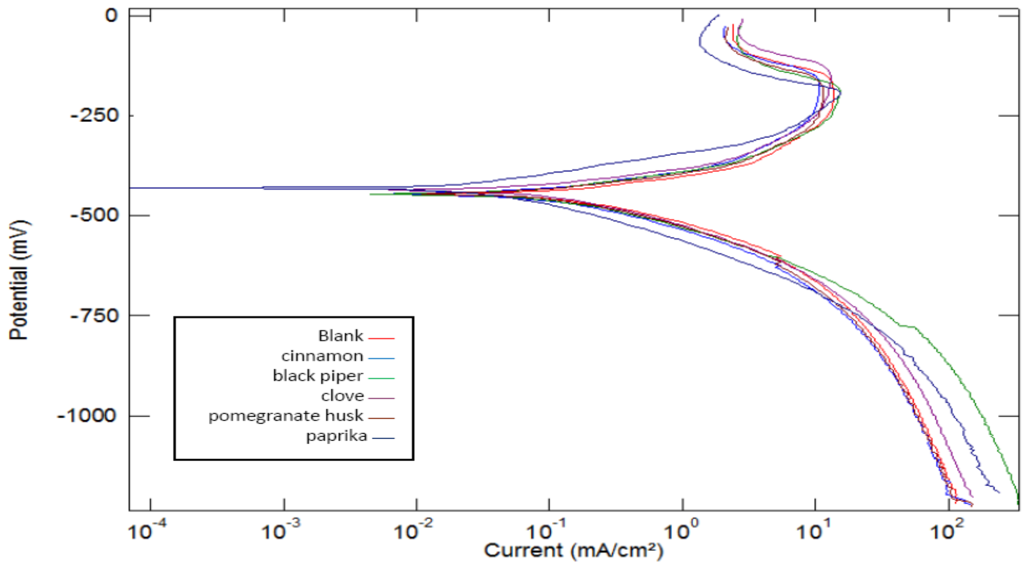

Fig. 2. Polarization curves for steel in 0.5 M HCl containing 300 ppm of Coriander extract and 87.5 ppm of different additives at 20˚C.

The values of C_{dl} are obtained at the frequency f_{max}, at which the imaginary component of the impedance is maximal, using the following equation:

$$C_{dl} = \frac{1}{2\pi \quad f_{\max} R_{ct}} \qquad (3)$$

The impedance diagram (Nyquist) Fig. 3 contains a depressed semicircle with the center under the real axis, such behavior characteristic for solid electrodes and often referred to frequency dispersion have been attributed to roughness and inhomogeneities of solid surface .The plots indicate that the process occurs under activation control. The diameter of Nyquist plots increases on increasing the Coriander extract concentration up to 900 ppm. These results suggested that the formed inhibitive film was strengthened as the concentration of Coriander extract was increased.

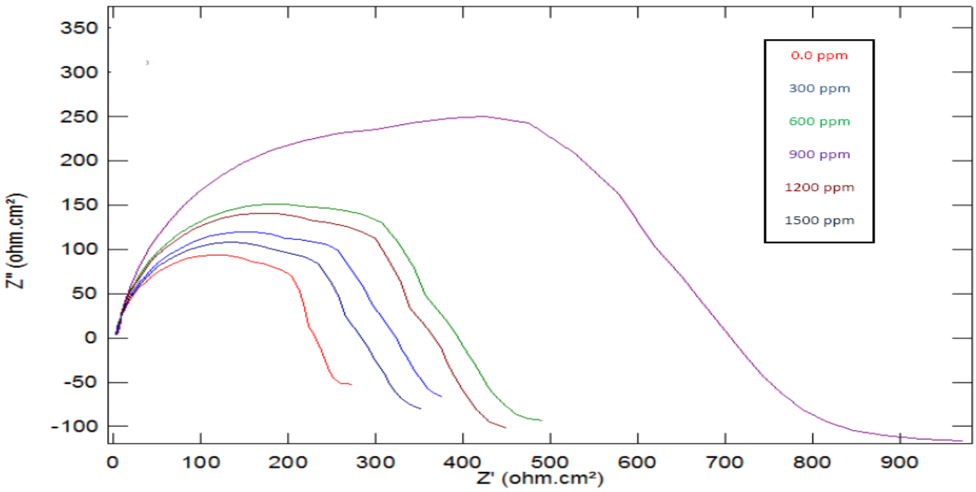

Fig. 3. EIS curves of steel in 0.5 M HCl at different concentrations of Coriander extracts at 20˚C.

On the other hand, the charge-transfer resistance R_{ct} increases and the pseudo capacity C_{dl} decreases on increasing Coriander extract concentration till 900 ppm which indicate that increases in concentration of

Coriander extract decreases corrosion rate and increases corrosion inhibition because the Coriander compounds inhibit the corrosion rate of steel by an adsorption mechanism [15, 16] this results confirms the results obtained above from the polarization measurements.
It is important to remark from table 3 that at inhibitor concentration (Coriander extract)>900 ppm, the inhibition of steel corrosion decreases again which indicated that the Coriander species may take part in catalyzing the hydrogen evolution reaction .

C (ppm)	$R_{ct(\Omega cm2)}$	$C_{dl(\mu F/cm2)}$	$f_{max(Hz)}$	θ	% IE
0	2.429	2.765	0.023709	0	0
300	2.994	2.173	0.024475	0.188711	18.87108
600	3.628	1.778	0.024685	0.330485	33.04851
900	5.491	1.554	0.018661	0.55764	55.76398
1200	3.336	1.489	0.032057	0.271882	27.18825
1500	2.627	2.192	0.027653	0.075371	7.537115

Table (3) Electrochemical impedance parameters for steel in 0.5 M HCl containing different concentrations of Coriander extracts at 20˚C.

Fig. 4 shows The Nyquist plots for steel in 0.5 M HCl solutions containing 300 ppm of aqueous extract of Coriander and 87.5 ppm with different additives. These plots have characteristic semicircles of a capacitive type whose size depends on the type and chemical constituent of the additive. The diameter of Nyquist plots increases with the following order:

Pomegranate husk≈ Black piper< Cinnamon≈ Clove< Paprika

The inhibition efficiencies, calculated from impedance results by using equation 2 are presented in Table 4 and show the same trend as those obtained from polarization studies . In fact, the presence of all additives with Coriander extract in an acidic solution increases the value of R_{ct} ,the effect being more pronounced with Paprika The order for additives similar to that obtained for the i_{corr} from polarization studies .

Table 4. Electrochemical impedance parameters for steel in 0.5 M HCl containing 300 ppm of the aqueous extract of Coriander and 87.5 ppm of different additives at 20˚C.

Additives+ Coriander in HCl(0.5M)	$R_{ct(\Omega cm2)}$	$C_{dl(\mu F/cm2)}$	$F_{max(Hz)}$	% IE
0	2.429	2.765	2.429	0
cinnamon+coriander	3.21	1.756	0.02825	24.33022
black piper+coriander	2.67	2.272	0.026249	9.026217
clove+coriander	3.201	2.437	0.020413	24.11746
pomegrnate husk+coriander	2.689	1.999	0.029624	9.669022
paprika+coriander	4.658	1.548	0.022084	47.85316

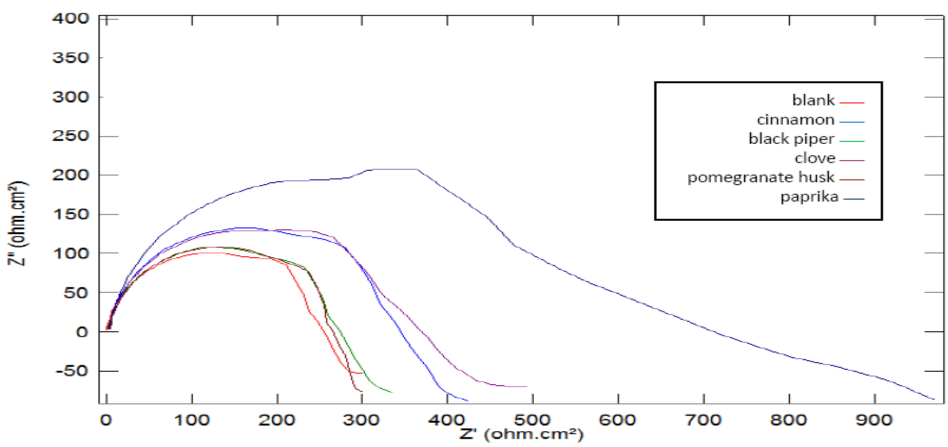

Fig. 4. Electrochemical impedance curves for steel in 0.5 M HCl containing 300 ppm of the aqueous extract of Coriander and 87.5 ppm of different additives at 20˚C.

3-3 Adsorption isotherm:

The adsorption mode of the inhibitors on the steel surface in the given medium must be defined by the relationship between the concentration of Coriander extracts (C) and the fraction of steel surface coverage (θ) by the adsorbed compound. The degree of surface coverage (θ) was calculated using the data obtained from electrochemical impendence measurement recorded in Table 3 using the following equation:

$$\theta = \frac{R_{ct\,(inh)} - R_{ct\,(acid)}}{R_{ct\,(inh)}} \quad (4)$$

The data were tested graphically, The best fit was obtained for the relation between C_{inh}/θ and C which represented in Fig. 5. The data indicate that the adsorption process follows Langmuir adsorption isotherm. The plot is linear with slope of (0.0008) and high correlation coefficient (0.9753).

Langmuir adsorption isotherm could be represented using the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (5)$$

where K_{ads} is the equilibrium constant of the adsorption process[17-18].

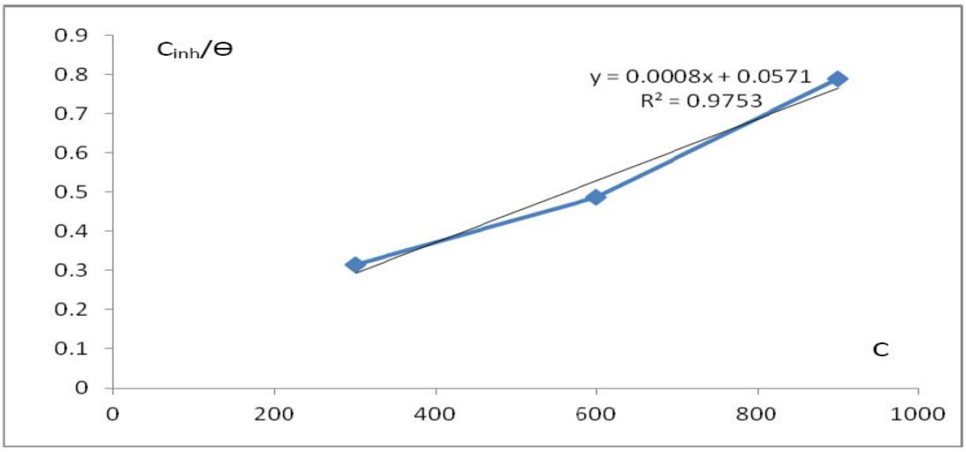

Fig. 5. Langmuir adsorption plot of Coriander extracts on steel in 0.5 M HCl at 20˚C.

3.4. Effect of temperature

The effect of temperature on the corrosion parameters of steel in free and inhibited solution of 0.5 M HCl was studied using polarization technique in the range of 20–50 ◦C Fig. 6. The acid solutions were inhibited by addition of 300 ppm of Coriander extract. The obtained corrosion parameters calculated from the polarization curves are given in Table 5. Inspection of Table 5reveals that the corrosion rates of steel in both free and inhibited acid media increased as the temperature was increased but is more pronounced for the uninhibited acid solution. The inhibition efficiency of the Coriander extract depends upon the temperature and increases with temperature. The activation energies of the corrosion process in free and inhibited acid solution were calculated using the Arrhenius equation [19].

$$k = A.\exp(-\frac{E}{RT}) \quad (6)$$

where E_a is the activation energy, *A* is the frequency factor, *T* is the absolute temperature, *R* is the gas constant, and *k* is the rate constant, which is directly proportion to the corrosion current (I_{corr}). Plotting lnI versus 1/*T* gives a straight line, as revealed from Fig. 7. The values of activation energy calculated using the lines of Fig. 7are 43.66kJmol^{-1},26.94kJmol^{-1} for free and inhibited acid solutions, respectively. The activation energy in presence of inhibitor is lower than in absence of inhibitor which means the possibility of increase in the corrosion current in the presence of Coriander extract , but it has been observed in the present case that in presence of inhibitor the corrosion current density is decreased , which indicates the change in the mechanism of the corrosion process when inhibitor is used [20-22] ,where it was attributed to be due to the chemical nature of interaction between inhibitor molecules and the steel surface .

Table (5) Corrosion parameters obtained from polarization curve of steel in 0.5 M HCl containing 300 ppm of Coriander extract at different temperatures.

T°C	Solution	E_{corr}(mV)	I_{corr}(mA/cm^2)	-b_c (mV)	b_a(mV)	% IE
20	Free	-449.69	1.95	163.62	89.77	——
	Inhibited	-433.64	1.28	156.09	104.18	34.35
30	Free	-448.09	3.41	144.3	104.76	——
	Inhibited	-439.64	2.78	195.91	168.05	18.47
40	Free	-422.41	8.07	148.25	134.17	——
	Inhibited	-416.37	3.67	171.83	138.21	54.52
50	Free	-421.45	9.23	186.39	145.18	——
	Inhibited	-413.51	4.01	178.16	144.5	56.55

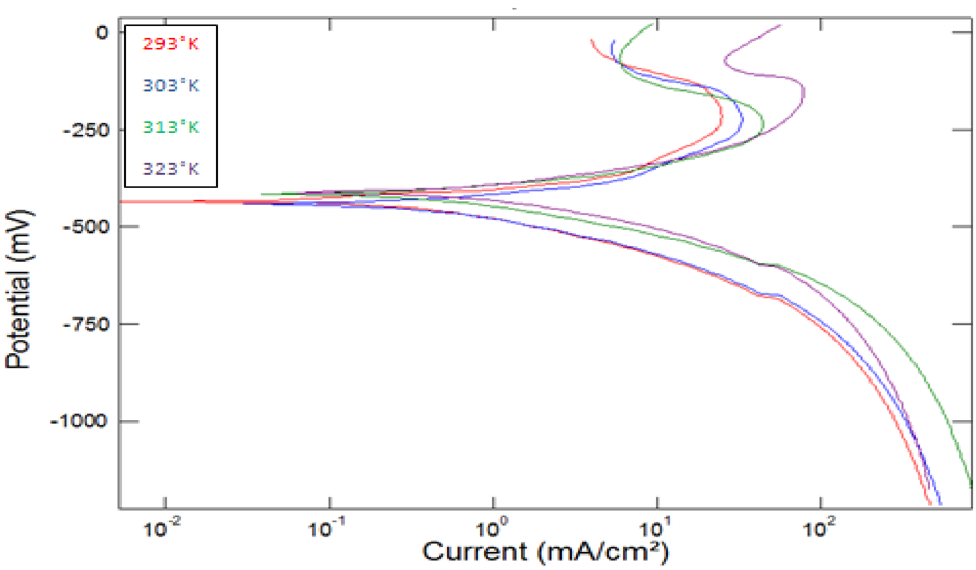

Fig. 6. Polarization curves for steel in 0.5M HCl + 300 ppm of Coriander extract under various temperature.

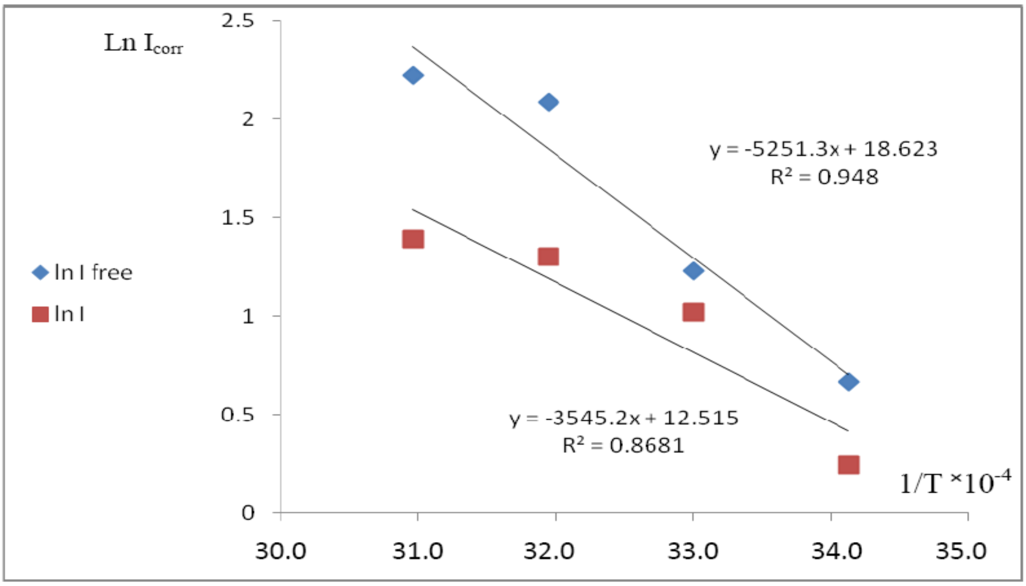

Fig. 7. Relationship between temperature and corrosion current density.

Conclusion

- The aqueous extract of Coriander (*Coriander sativum*) acts as a good inhibitor for the corrosion of steel in 0.5 M HCl.
- The inhibition efficiency of the inhibitor increases with the concentration up to the critical concentration 900 ppm.
- The addition of some additives supported the corrosion inhibition action of Coriander in acidic media with the flowing order :
  Paprika > Clove>Cinnamon > Black piper > Pomegranate husk
- Aqueous extract of Coriander (*Coriander sativum*) acts as a mixed inhibitor.
- The adsorption process of the Coriander inhibitior follows Freundlich adsorption isotherm

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