

Effect of Ajowan Seeds as Safe Inhibitor on the Corrosion of Steel in 2.0 M Sulfuric Acid

BY:

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Abstracts

Corrosion inhibition of steel in sulphuric acid by aqueous extract of *Ajowan* (*carum*) seeds has been studied using chemical (HE and ML) and electrochemical (EIS and PDP) measurements at 30°C. The results indicated that *Ajowan* extract inhibit the corrosion process in 2.0M H₂SO₄ and the inhibition efficiency increase as concentration increased. Impedance studies showed that the charge transfer controls the dissolution mechanism of steel across the phase boundary in the absence and the presence of the inhibitor and potentiodynamic polarization results indicate that *Ajowan* seeds act as mixed type inhibitor. The inhibition efficiency obtained from various employed methods is approximately in good agreement. Adsorption process of *Ajowan* molecules on steel surface is spontaneous and it obeys the Freundlich adsorption isotherm.

Key words: *Ajowan* plant, corrosion, inhibition, steel, acids, sulphuric acid.

1 Introduction:

Steel is considered to be the main constructing materials in industry. There is a great need to protect steel from dissolution by using corrosion inhibitors. Acid scaling and corrosion inhibitors find wide applications in the industrial field as a component for industrial equipments, and in acidization of oil wells⁽¹⁾.

Many studies have been made on the corrosion inhibition of steel in acid media⁽²⁻⁶⁾. Many of the commonly used inhibitors are organic compounds that can be hazardous to health if they are allowed to contaminate the environment.

Due to the currently imposed environmental requirements for friendly corrosion inhibitors, there is a growing interest in the use of natural products such as leaves or seeds extract. Natural plant extract represent a category of non- toxic and have safe chemical compounds that can be extracted by simple procedures with low cost and used as corrosion inhibitors.

A recent trend is devoted to employ the extracts of natural compounds as novel corrosion inhibitors of metals in different media⁽⁷⁻¹⁴⁾.

Ajowan plant (*carum*), Fig.(1a and b) is organic in nature and is much used as a medical plant in Ayurvedic medicine, mainly, it helps against diseases of the digestive tract and fever. *Ajowan* seeds(Fig.1b) contain of a volatile oil which contain of Thymol(39.36%), γ -Terpinene(30.97%), *p*-Cymene(19.47%), β -Pinene(5.45%), α -Pinene(1.48%) and Limonene⁽¹⁵⁾. Figure (2) illustrates the structures of some of the major compounds in *Ajowan* seeds.

The purpose of this paper is to elucidate the corrosion inhibition of steel in sulphuric acid by *Ajowan* seeds extract as safe and novel inhibitor.

2 Experimental:

2.1 Preparation of the Plant Extract

Stock solution of the extract of *Ajowan* (*carum*) plant were prepared by boiling 20g. of *Ajowan* seeds in 250ml. of bi-distilled water for 1.0 hour and left all night, then it filtered and completed to 250ml. by bi-distilled water in measuring flask. The extract then is kept the solution in refrigerator at low temperature. The concentration of all additives were expressed in %v/v.

2.2 Preparation of the Metal Specimen

Commercial steel electrode with the chemical composition 0.38% C, 0.15% Mo, 0.50% Mn, 0.40% Si, 0.03% S, 0.035% P and 97.61% Fe was used, it polished using different emery papers up to 1200 grade, washed thoroughly with bi-distilled water degreased with acetone and dried.

2.3 Electrolyte

The solution used were made of AR grade sulphuric acid. Appropriate concentration of acid was prepared by using bi-distilled water. The concentration range of the inhibitor (*Ajowan* extract) employed was varied from 1.0 to 15.0%v/v.

2.4 Chemical and Electrochemical Measurements

A chemical (hydrogen evolution and mass loss) measurements were carried out as described elsewhere⁽¹⁶⁾. Electrochemical (impedance and polarization) measurements were carried out using an impedance spectrum analyzer (ACM instrument) connected to a Samsung computer (Bridgmax DVD ASUS 8X)⁽¹⁷⁾. The input signal amplitude was 10 mV peak to peak in both high and low frequency ranges. The electrode potential was measured against silver/silver chloride electrode. A platinum foil was used as an auxiliary electrode.

The inhibition efficiency from chemical methods ($\text{Inh}_{\text{HE}}\%$ and $\text{Inh}_{\text{MS}}\%$) and electrochemical methods ($\text{Inh}_{\text{EI}}\%$ and $\text{Inh}_{\text{P}}\%$) were calculated from the following relations, respectively:

$$\text{Inh}_{\text{HE}}\% = (1 - R / R_o) \times 100 \quad (1)$$

$$\text{Inh}_{\text{ML}}\% = (1 - R' / R_o) \times 100 \quad (2)$$

$$\text{Inh}_{\text{EI}}\% = (1 - 1/R_{\text{ct}} / 1/R_{\text{ct}}^o) \times 100 \quad (3)$$

$$\text{Inh}_{\text{P}}\% = (1 - I_{\text{corr}} / I_{\text{corr}}^o) \times 100 \quad (4)$$

where, R , R_o , R' , R_o , I_{corr} , I_{corr}^o , R_{ct} and R_{ct}^o are the corrosion rate, the corrosion current and the charge transfer resistance for steel in absence and presence of certain concentrations of *Ajowan* extract from HE, ML, EI and P methods, respectively.

3 Results and Discussion:

3.1 Hydrogen Evolution and Mass Loss Study

The corrosion rates for steel in 2.0M H₂SO₄ in absence and presence of *Ajowan* extract were determined using hydrogen evolution (HE) and mass loss (ML) methods.

Figure (3) shows the plots of the variation of hydrogen gas evolved with time during the corrosion of steel in 2.0M H₂SO₄ at various concentrations of *Ajowan* extract at 30° C.

Inspection of the plots reveals that hydrogen gas evolution commences only after an induction period, which corresponds to the time interval needed by the corrodent to break down the pre-immersion oxide film on the steel surface⁽¹⁸⁻²⁵⁾. After the induction period, the volume of evolved H₂ gas varies linearly with reaction time. The plots also illustrate the decreased deflection of H₂ gas evolution rate on introduction of the extract into the corrodent, indication that the *Ajowan* extract affords corrosion inhibition of steel in the acidic environment. The volume of H₂ evolved were observed to reduce on addition of different concentrations of *Ajowan* extract. This indicates that *Ajowan* plant extract inhibits the corrosion of steel in 2.0M H₂SO₄ and suggesting that the inhibiting action was concentration dependent.

The corrosion rates obtained from HE and ML methods for the corrosion of steel in presence of different concentrations of *Ajowan* extract in 2.0M H₂SO₄ were assessed from the slopes of the linear portions of the hydrogen evolution plots and from the relation ($R' = (W_1 - W_2)/t \times A$), respectively, where W₁ and W₂ are the weighed of steel before and after immersion, A is the area of steel sample and t is the immersion time. The corresponding values of corrosion rate for the different test solutions are given in Table (1).

The results show that the corrosion rates from HE and ML measurements decreased with increasing the extract concentration and the values of inhibition efficiency (Inh._{HE}% and Inh._{ML}%) increase with increasing *Ajowan* extract concentration (Table 3). This behavior may be attributed to the increase of the surface area covered by the adsorbed molecules of *Ajowan* extract with the increase in concentration of the inhibitor. In *Ajowan* seeds organic compounds present such as Thymol, γ -Terpinene, *p*-Cymene, β -Pinene, α -Pinene and Limonene atc , can easily be adsorbed on steel surface giving rise to inhibition and the inhibition may be due to their synergistic action of these compounds.

3.2 Impedance and Potentiodynamic Polarization Study

Nyquist diagrams over a wide range of frequency were obtained after 20 min. immersion of steel sample in 2.0M H₂SO₄ in the absence and presence of different concentrations of *Ajowan* extract at 30° C are shown in Figure (4).

As can be notice from Figure (4), the impedance diagrams obtained were not perfect semicircles, this difference has been attributed to frequency dispersion⁽²⁶⁾. The semi-circles appearance indicating a charge transfer process mainly controlling the corrosion of steel in 2.0M H₂SO₄ and the presence of the extract of *Ajowan* plant in acidic solution does not alter the mechanism of dissolution of steel surface⁽²⁷⁾.

The potentiodynamic polarization curves are presented in Figure (5), the corresponding polarization curves exhibit Tafel type behavior and *Ajowan* extract retard both anodic and cathodic processes (metal dissolving and hydrogen evolution), this appears in the displacement of Tafel lines (cathodic and anodic), i.e., *Ajowan* extract act as mixed type inhibitors. The electrochemical parameters obtained from impedance and polarization curves are summarized in Table (2). These include, the charge-transfer resistance (R_{ct}) which calculated from the

difference in impedance at lower and higher frequencies, as suggested by Tsuruta et al.⁽²⁸⁾ and the double layer capacitance (C_{dl}) values which obtained from equation:

$$C_{dl} = \pi f_{max} R_{ct} / 2 \quad (5)$$

where f is the frequency at the maximum height of the semi-circle on the imaginary axis, the corrosion potential (E_{corr}), the corrosion current (I_{corr}), the anodic and cathodic Tafel constants (b_a and b_c), for *Ajowan* extract.

As can be seen, the presence of *Ajowan* extract enhances the value of R_{ct} in acidic solution 2.0M H_2SO_4 , the values of R_{ct} increases with the increase in concentration of *Ajowan* extract. Also, values of double layer capacitance are decreases in the presence of extract. The decrease in C_{dl} is suggested to be due to the adsorption of *Ajowan* compounds on the steel surface leading to the formation of film from acidic solution⁽²⁹⁾. It is also noted that the presence of *Ajowan* extract has a pronounced effect on the corrosion current and shifts the corrosion potential by ≈ 20 mV to more negative values and it remain approximately constant by increasing the *Ajowan* extract concentration. *Ajowan* extract affects both anodic and cathodic over potentials, i.e. acting as mixed type inhibitor by forming an adsorbed layer at the metal/solution interface that decreases the available anodic and cathodic sites required for metal dissolution and hydrogen evolution, respectively.

3.3 Inhibition Efficiency and Adsorption Isotherm

The inhibition efficiency got from chemical (HE and ML) and electrochemical (EI and P) methods are listed in Table (3). It is clear that the inhibition efficiencies in presence of *Ajowan* extract increase with increasing the concentration of extract up to 5.0%v/v. Above that level, increasing the concentration from 5.0%v/v to 15.0%v/v has a little effect on the inhibition efficiency of steel corrosion by *Ajowan* extract. This behavior could be attributed to the synergistic effect of the major chemical constituents of *Ajowan* extract (Fig.(2)) leading to cover anodic and cathodic sites through their oxygen function groups (OH). The larger number of different chemical compounds for *Ajowan* extract (AE) may react with the steel (iron, Fe), which is firstly dissolved from the metal surface, forming organo-metallic complex such as Fe-*Ajowan* extract $[Fe-AE]^{2+}$ according to the following mechanism⁽³⁰⁾



where Fe-*Ajowan* extract, $[Fe-AE]^{2+}$ may be as a stable complex adsorbed over the metal surface resulting an inhibitive effect.

Figure (6) shows the relationship between inhibition efficiency (Inh.%) and logarithm of concentration (log C) of *Ajowan* extract in 2.0M H_2SO_4 from chemical and electrochemical methods. It is clear that the results approximately in agreement but there are some difference in the values of inhibition efficiency from all methods. The difference observed can be attributed to the difference in measurement methods and to the fact that the chemical methods give average corrosion rates, whereas electrochemical methods give instantaneous corrosion rates⁽³¹⁾. As can be readily seen from Figure (6), all plots have the form of S-shaped adsorption isotherm. This indicates that corrosion inhibition process occurs by adsorption. To know the mechanism of electrochemical reaction, it is necessary to select the appropriate adsorption isotherm. It is found from the results in Figure (7) that the adsorption of extract followed the Freundlich adsorption isotherm using the following equation^(32,33):

$$\Theta = K C^n$$

(6)

$$\log \Theta = \log K + n \log C$$

(7)

where, $0 < n < 1$, Θ is the degree of surface coverage for different concentrations of *Ajowan* extract, C is the *Ajowan* extract concentration and K is the bonding constant (equilibrium constant) of the adsorption process.

It is clear from Figure (7), that the relation between $\log \Theta$ vs. $\log C$ give a straight lines from all methods which indicates that the adsorption of *Ajowan* extract molecules on the steel surface obey Freundlich isotherm.

The standard free energies for adsorption was calculated using the equation (8):

$$\log K = \log (1 / 55.5) - \Delta G_{\text{ads}}^{\circ} / 2.303RT$$

(8)

where the numerical value (1/55.5) stands for molarities of water, the calculated values of $-\Delta G_{\text{ads}}^{\circ}$ are 6.553, 7.958, 7.055 and 8.029 kJ./mol. from HE, ML, EI and P methods, respectively which are low values, indicating that the interaction between *Ajowan* molecules and the steel surface is found by the physical adsorption which is the result of electroactive forces between oxygen atom with lone pair of electrons on the *Ajowan* molecules and the electrically charged surface of the steel. The negative sign of free energy of adsorption indicates that the adsorption of *Ajowan* extract at steel surface is a spontaneous process ^(14,34-36).

Conclusion:

From the present investigation, the following conclusions can be drawn:

- *Ajowan* seeds extract was found to be good nontoxic and safe inhibitor for steel corrosion in 2.0M H₂SO₄.
- The chemical and electrochemical measurements showed that inhibition efficiency increased with an increase in *Ajowan* extract concentration.
- EIS shows that the charge-transfer resistance increases by increasing the concentration of the *Ajowan* extract, while the capacitance of double layer decreases with increasing the extract concentration.
- The electrochemical results from potentiodynamic polarization indicate that the *Ajowan* extract affected both anodic and cathodic processes i.e., *Ajowan* extract is mixed type inhibitor.
- The corrosion process is inhibited by adsorption of *Ajowan* molecules on steel surface following the Freundlich isotherm and the adsorption is physical.

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Table 1: Corrosion rates obtained from HE and ML for steel in 2.0M H₂SO₄ in absence and presence of different concentrations of **Ajowan** extract at 30 ° C.

C _{inh} .v/v%	0.0	1.0	2.0	5.0	10.0	15.0
R x 10 ² (ml.cm ⁻² min)	4.000	2.960	2.467	1.180	0.933	0.457
R' x 10 ⁵ (g.cm. ⁻² min)	6.673	5.911	5.222	3.330	2.248	1.952

Table (2): Electrochemical parameters for steel corrosion in 2.0M H₂SO₄ in presence of different concentrations of **Ajowan** extract at 30 ° C.

C %v/v	Impedance			Polarization				
	R _{sol} . Ohm cm ²	R _{ct} Ohm cm ²	C _{dl} x10 ⁻⁴ F	-E _{corr} . (mv)	b _a V/dec.	b _c V/dec.	I _{corr} . mA/cm ²	R _{corr} . mm/dey
0.0	0.939	9.134	0.205	404.16	58.408	102.57	8.0176	92.925
1.0	1.217	10.32	8.770	424.66	28.567	100.52	5.1296	59.453
2.0	1.190	15.94	7.104	424.31	17.346	127.23	4.6532	53.931
5.0	1.040	20.28	6.078	422.10	35.662	75.909	4.0978	47.493
10.0	1.442	22.67	3.449	425.15	34.689	26.474	3.4317	39.779
15.0	1.278	23.39	2.302	411.46	32.357	101.08	2.4298	28.161

Table 3: The inhibition efficiencies (Inh.%) for steel corrosion in 2.0M H₂SO₄ in presence of **Ajowan** extract at 30 ° C from different methods.

C %v/v	Inhibition%			
	Inh. _H	Inh. _M	Inh. _{Rct}	Inh. _p
0.0	--	--	--	--
1.0	26.00	11.42	11.51	36.02
2.0	38.33	21.74	42.74	41.96
5.0	70.50	50.10	54.98	48.89
10.0	76.67	66.31	59.73	57.20
15.0	88.57	70.75	60.91	69.69

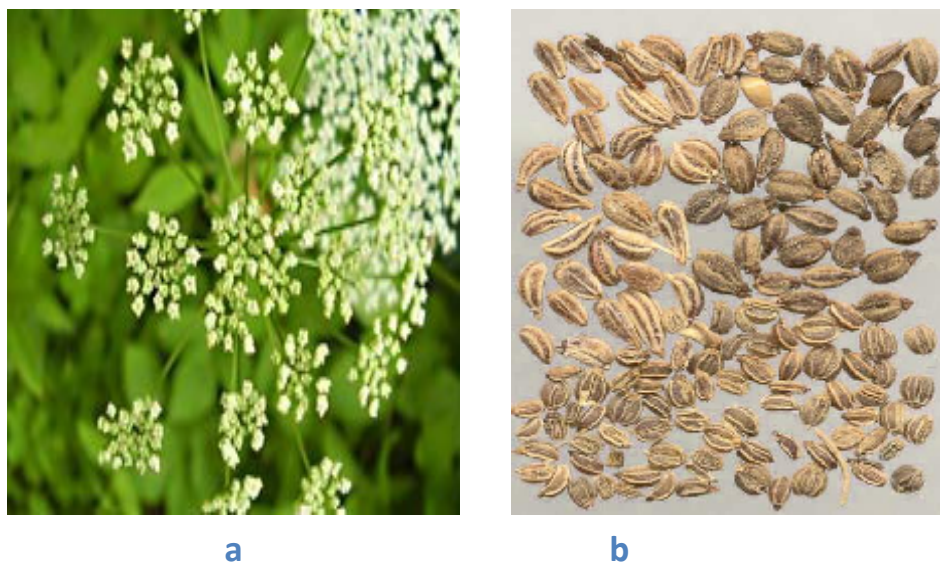


Figure 1. **Ajowan**(carum) plant **a)**Tree and **b)**Seeds.

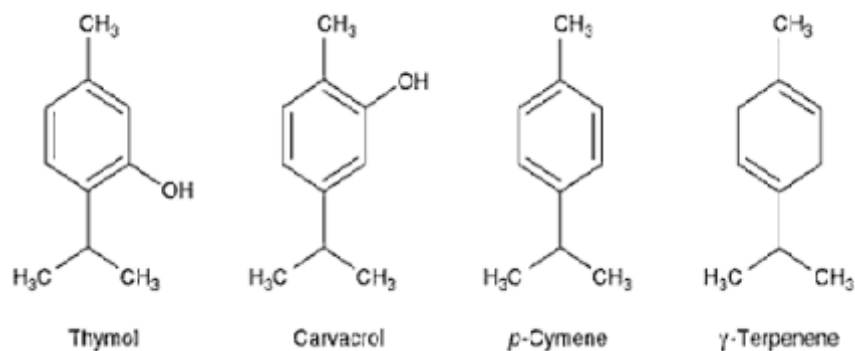


Figure 2. Structure of some **Ajowan** components.

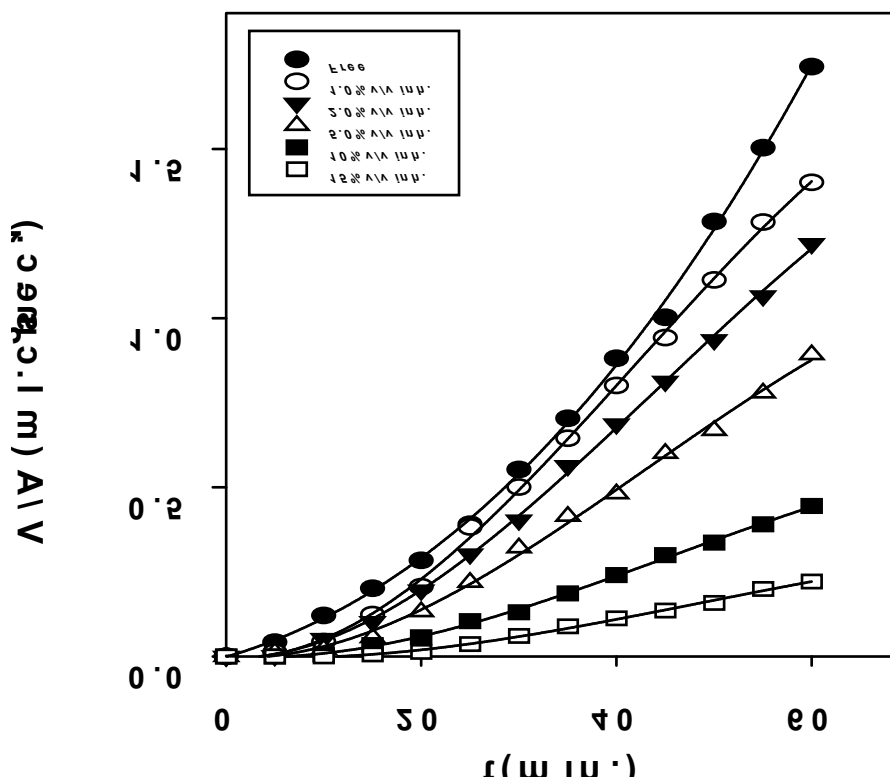


Figure 3. Hydrogen/time curves for steel sample corrosion in 2.0M H₂SO₄ in absence and presence of different concentrations of **Ajowan** plant extract at 30°C.

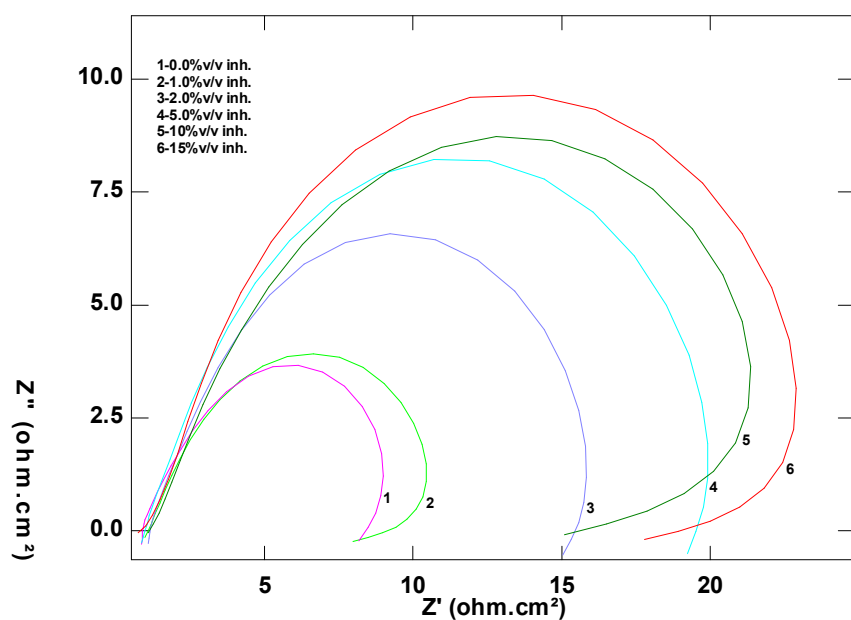


Figure 4. Nyquist plots of steel sample corrosion in H_2SO_4 in absence and presence of different concentrations of **Ajowan** plant extract at $30^\circ C$.

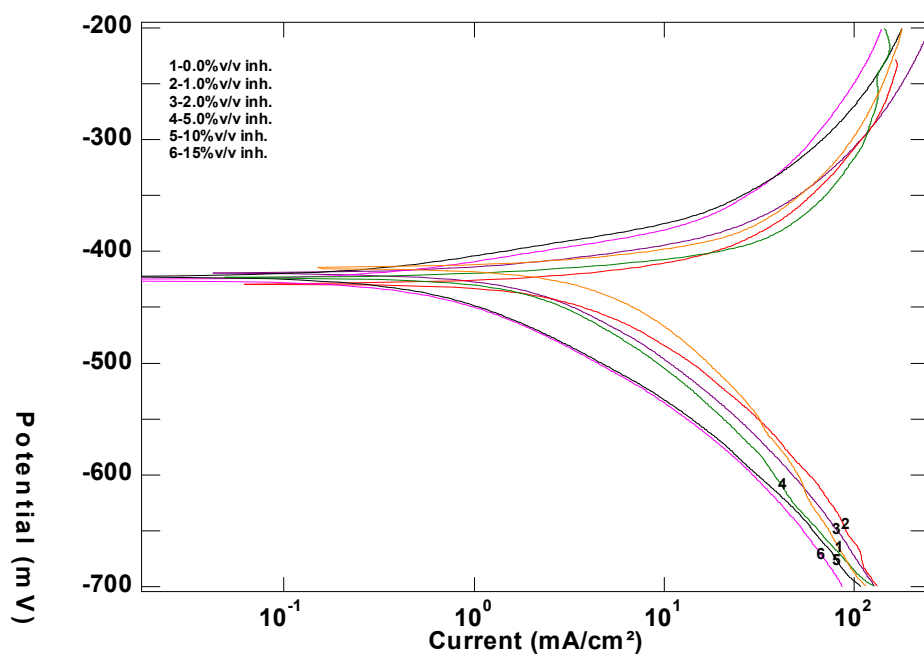


Figure 5. Polarization plots for steel sample corrosion in $2.0M H_2SO_4$ in absence and presence of different concentrations of **Ajowan** plant extract at $30^\circ C$.

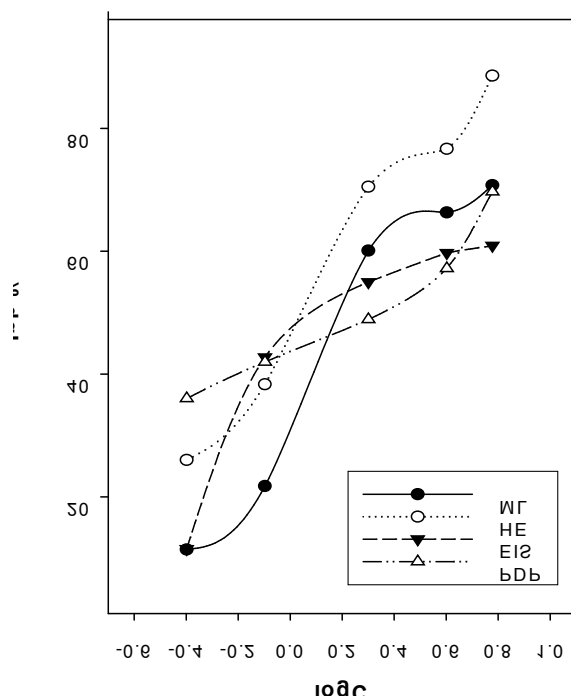


Figure 6. The variation of inhibition efficiency (Inh.%) against $\log C_{inh}$ for steel corrosion in 2.0M H_2SO_4 at 30°C.

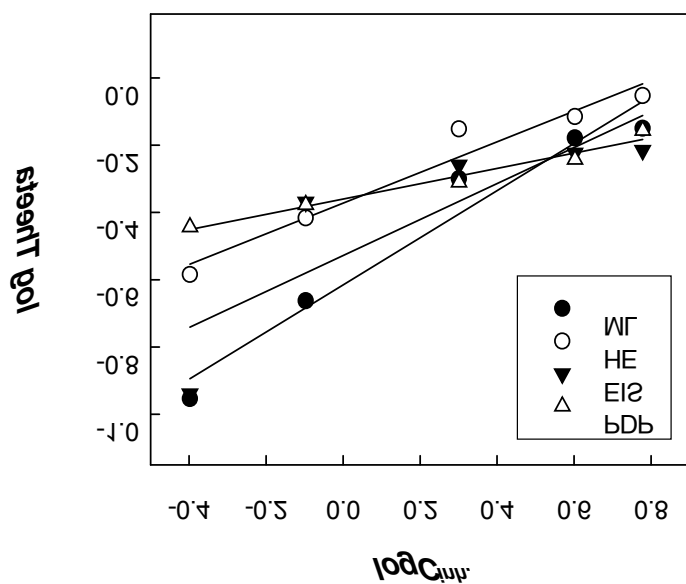


Figure 9. Freundlich adsorption plots for the extract of **Ajowan** plant extract
2.0M H_2SO_4 at 30 °C.