

Short Communication

Study of the Corrosion Inhibition Effect of Pistachio Essential Oils in 0.5 M H₂SO₄

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The corrosion inhibition of Pistachio Essential Oils (**PEO**) on carbon steel in 0.5 M H₂SO₄ was investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Results showed that **PEO** inhibited carbon steel corrosion in a 0.5 M H₂SO₄ solution and indicated that the inhibition efficiencies increased with the concentration of inhibitor. Potentiodynamic polarization studies suggested that this inhibitor is a mixed type inhibitor with predominance anodic type. Nyquist plots indicated that the addition of inhibitor decreases the double-layer capacitance (C_{dl}) of the corrosion process depressed semicircles with their centre below real axis. The PEO adsorption on the carbon steel surface followed the Langmuir adsorption isotherm.

Keywords: carbon steel, inhibition, pistachio essential oils, EIS, Potentiodynamic polarization, Langmuir.

1. INTRODUCTION

Steel is widely used in most industries because of its low cost and availability for the manufacture of reaction vessels such as cooling tower reservoirs, pipelines, etc...[1]. Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes.

Hydrochloric and sulfuric acids are widely used in the pickling processes of metals [2]. Organic compounds containing heteroatoms are commonly used to reduce the corrosion attack on steel in acidic media. Overall, these compounds adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion process [3-8]. The toxic nature of these organic inhibitors has required research activities in recent times toward finding alternative environmentally friendly acid corrosion inhibitors. These advantages have incited us to draw a large part of program of our laboratory to examine natural substances as corrosion inhibitors such as : Menthols [9], Rosemary oil [10-12], Thymus oil [13-14], Artemisia [15,17], carob seed oil [16], Argan hulls extract [18], Eugenol and Acetylugenol [19], Ginger [20], Lavender oil [21], Limonene [22], Pulegone and Pulegone oxide [23], Jojoba oil [24] and *Bifurcaria bifurcata extract* [25]. *Salvia aucheri mesatlantica* [26], Pennyroyal Mint oil [27], *verbena essential oils* [28], Argania plant extract [29] and Argan Press Cake Extract [30]. The encouraging results obtained by naturally oils as corrosion inhibitor of steel in acid solutions permit to test more substance oils. The objective of this study was to find an environmentally safe and inexpensive inhibitor (pistachio essential oils) of corrosion of C38 steel in acidic solution by polarization, electrochemical impedance spectroscopy (EIS) and weight loss measurements.

2. MATERIALS AND METHODS

2.1. Oil distillation

The ripe fruits was purchased from retail in Agadir (Morocco). It was identified at autonomous establishment of control and export coordination. A voucher specimen sample was deposited in the Herbarium of the Laboratory of Environmental Engineering and Biotechnology. The aerial parts of the plant were air-dried in the laboratory at room temperature. A sample of 200 g was subjected to water distillation for two hours using a Clevenger-type apparatus recommended by the French Pharmacopoeia [31]. The yield was determined as grams over the 200 g of powder analyzed in percentage, and is shown in Table 1. The oil was analyzed using a Hewlett-Packard 5972 MS, fitted with a HP 5890 Series II GC, and controlled by a G1034C Chemstation. A sample of 1ml was injected under the following conditions: DB-1 fused silica capillary column (20 m x 0.20 mm, film thickness 0.2 mm); carrier gas helium (0.6 ml/min); injector temperature 250°C; column temperature 50- 250°C at 3°C/min; and MS electronic impact 70 eV. The identification of the compounds was achieved by comparing retention times and mass spectra with those of the published standards [32-33].

2.2. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltmaster software. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working

electrode having composition: 0.179% C, 0.165% Si, 0.439% Mn, 0.203% Cu, 0.034% S and Fe balance. Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers. The surface area exposed to the electrolyte is 0.04 cm².

Potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5 mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarization curves are obtained from -800 mV to -200 mV at 298 K. The solution test is there after de-aerated by bubbling nitrogen. Gas bubbling is maintained prior and through the experiments. In order to investigate the effects of temperature and immersion time on the inhibitor performance, some test were carried out in a temperature range 298–328 K.

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the same electrochemical system. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

2.3. Weight loss measurements

Coupons were cut into 2 × 2 × 0.08 cm³. Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water, degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 80 cm³. The immersion time for the weight loss is 6 h at 298K.

3. RESULTS AND DISCUSSION

3.1. Pistachio essential oil analysis

The chemical analysis of PEO of the unripe fruits showed that it was rich in α -pinene (54.2%) and terpinolene (32.2%). β -pinene, limonene and 3-carene not exceeding 1%.

3.2. Effect of concentration

3.2.1. Polarization curves

Fig. 1 shows the potentiodynamic polarization curves after the addition of corrosion inhibitor **PEO**. In every curve, it is observed that the current densities of the anodic and cathodic branch are displaced towards lower values. This displacement is more evident with the increase in concentration of the corrosion inhibitor when compared to the blank material.

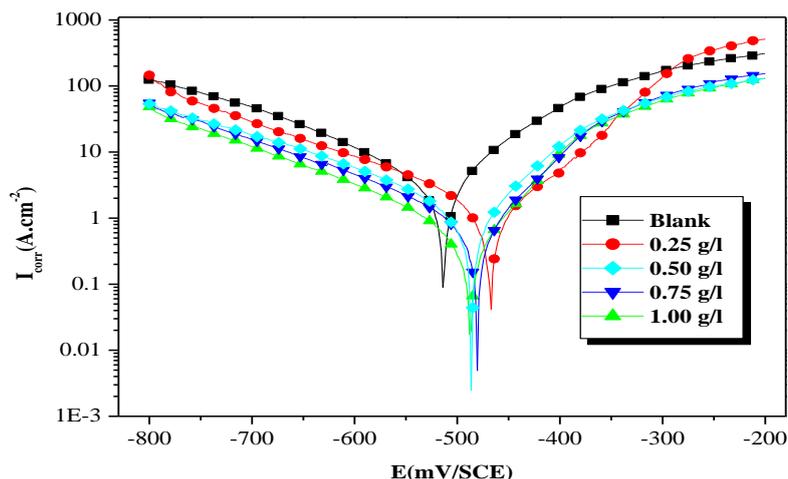


Figure 1. Potentiodynamic polarization curves of carbon steel in 0.5 M H₂SO₄ in the presence of different concentrations of **PEO**.

The inhibition efficiencies were calculated from I_{corr} values according to following equation [35-36]:

$$IE \% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \tag{1}$$

Where I_{corr} and I'_{corr} are the corrosion current densities in the absence and the presence of the inhibitor.

The Table 1 gives the values of kinetic corrosion parameters as the corrosion potential E_{corr} , corrosion current density I_{corr} , cathodic Tafel slope (b_c), and inhibition efficiency for the corrosion of carbon steel in 0.5 M H₂SO₄ with different concentrations of **PEO**. The corrosion current densities were estimated by Tafel extrapolation of the cathodic curves to the open circuit corrosion potentials.

Table 1. Electrochemical parameters of carbon steel at various concentrations of **PEO** in 0.5 M H₂SO₄ and corresponding inhibition efficiency.

Inhibitor	Conc (g/L)	E_{corr} (mV/SCE)	I_{corr} (mA/cm ²)	- b_c (mV/dec)	$IE_{I_{corr}}$ (%)
Blank	0.0	-513	3.9579	205	-
PEO	0.25	-467	1.9608	177	50.45
	0.5	-487	1.4150	190	64.24
	0.75	-482	1.0832	197	72.63
	1.00	-488	0.7265	173	81.64

In acidic solutions, the anodic reaction of corrosion is the passage of metal ions from the metal surface into the solution, and the cathodic reaction is the discharge of hydrogen ions to produce hydrogen gas or to reduce oxygen [37-39]. In every curve, it is observed that the current densities of

the anodic and cathodic branch are displaced towards lower values. This displacement is more evident with the increase in concentration of the corrosion inhibitor when compared to the blank material. From Table 1, the corrosion current density decreased with the increase of the inhibitor concentration. These results indicated that the presence of **PEO** inhibited both iron oxidation and hydrogen evolution, consequently **PEO** can be classified as mixed corrosion inhibitor [40].

3.2.2. Electrochemical impedance spectroscopy measurements:

Fig. 2 shows the Nyquist diagrams for mild steel in 0.5 M H₂SO₄ at 298K after immersion of 30 min containing various concentrations of **PEO**.

From this figure, we can see that all The impedance spectra exhibit one single depressed semicircle, and the indicates that the charge transfer takes place at electrode/solution interface, and the transfer process controls corrosion reaction of steel and the presence of inhibitor does not change the mechanism of steel dissolution [41].

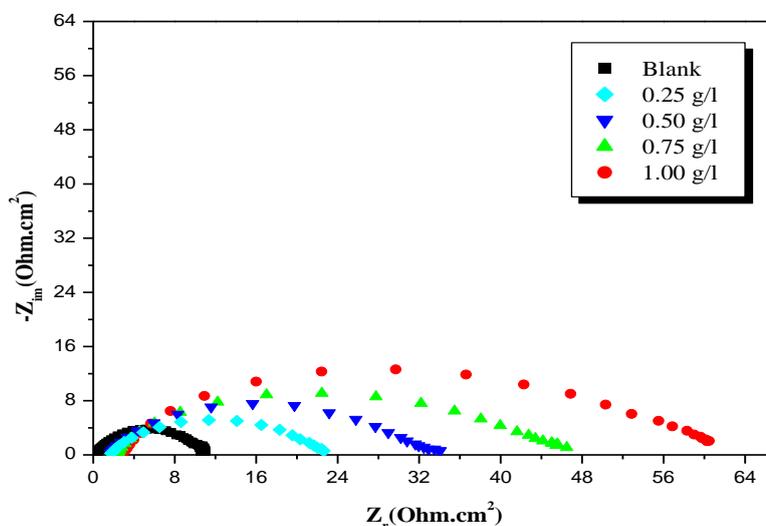


Figure 2. Nyquist diagrams for carbon steel electrode with and without **PEO** at E_{corr} after 30 min of immersion

Also, these impedance diagrams are not perfect semicircles which are related to the frequency dispersion as a result of the roughness and inhomogeneous of electrode surface [42]. Furthermore, it is apparent, from these plots that, the impedance response of mild steel in uninhibited H₂SO₄ solution has significantly changed after addition of **PEO** in the corrosive solution; as a result, real axis intercept at high and low frequencies in the presence of inhibitor is bigger than that in the absence of inhibitor (blank solution) and increases as the inhibitor concentration increases. This confirms that the impedance of inhibited substrate increases with the concentration of **PEO** in 0.5 M H₂SO₄. The electrochemical parameters are summarised in Table 2.

The inhibition efficiency is calculated by charge transfer resistance as follows [37]:

$$IE_{R_t} \% = \frac{R_t^0 - R_t}{R_t^0} \times 100 \quad (2)$$

where R_t^0 and R_t are the charge transfer resistance values without and with inhibitor for carbon steel in acidic media, respectively.

Table 2. Electrochemical Impedance parameters for corrosion of carbon steel in 0.5 M H₂SO₄ at various contents concentrations of **PEO**.

Inhibitor	Conc (g/l)	R _t (Ω cm ²)	C _{dl} (μF cm ⁻²)	IE _{Rt} (%)
Blank	0.5 M	10	215.09	----
PEO	0.25	23	94.64	54.00
	0.5	34	48.12	68.88
	0.75	47	9.66	77.48
	1.00	63	5.61	83.20

As shown in Table 2, R_t values increases prominently while C_{dl} reduces with the concentration of **PEO**. The decrease in C_{dl} comparing with that in blank solution (without inhibitor), which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecules function by adsorption at the metal/solution interface [43]. IE_{R_t} (%) increases with the concentration of **PEO** and the maximum of inhibition reaches up to 83.2%, which further confirm **PEO** exhibits good inhibitive performance for mild steel in 0.5 M H₂SO₄.

3.2.3. Weight loss, corrosion rates and inhibition efficiency

The gravimetric measurements of mild steel in 0.5 M H₂SO₄ in the absence and presence of various concentrations of **PEO** investigated were determined after 30 min of immersion at 298K. The inhibition efficiency of the inhibitor for the corrosion of mild steel was calculated as follows [44].

$$IE_{wL} \% = \frac{W_0 - W_i}{W_0} \times 100 \quad (3)$$

and

$$\theta = \frac{W_0 - W_i}{W_0} \quad (4)$$

where, w_0 and w_i are the weight loss value in the absence and presence of inhibitor.

Table 3 gives values of the corrosion rates and percentage inhibition efficiency calculated from the weight loss measurements for different concentrations of **PEO**. The mild steel corrosion rate decrease with increasing concentration of inhibitors. At this purpose, one observes that the optimum concentration of inhibitor required to achieve the efficiency is found to be 1 g/l ($IE_{wL} = 87.12\%$).

It should be noted that the inhibition efficiencies obtained from electrochemical methods and weight loss measurements are in good reasonably agreement.

Table 3. Corrosion rates and inhibition efficiencies of **PEO** at different concentrations in 0.5 M H₂SO₄.

Inhibitor	Conc (g/l)	C _R (mg cm ⁻² h ⁻¹)	μ _{WL} (%)	θ
Blank	0.5 M	1.790	---	---
PEO	0.25	0.8706	51.36	0.5136
	0.5	0.6529	63.52	0.6352
	0.75	0.4500	74.86	0.7486
	1.00	0.2305	87.12	0.8712

3.3. Adsorption isotherm

Assuming the increase of the inhibition is caused by the adsorption of inhibitor on the surface and obeys Langmuir adsorption isothermal equation [45-46]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{5}$$

where C_{inh} is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant and θ is the surface coverage calculated from weight loss measurement

Plotting C/θ versus C yields a straight line as shown in Fig.4. The linear correlation coefficient (r) is almost equal to 1 (r = 0.9999) and the slope is very close to 1 (slope = 0.98), indicating the adsorption of **PEO** on steel surface obeys Langmuir adsorption isotherm.

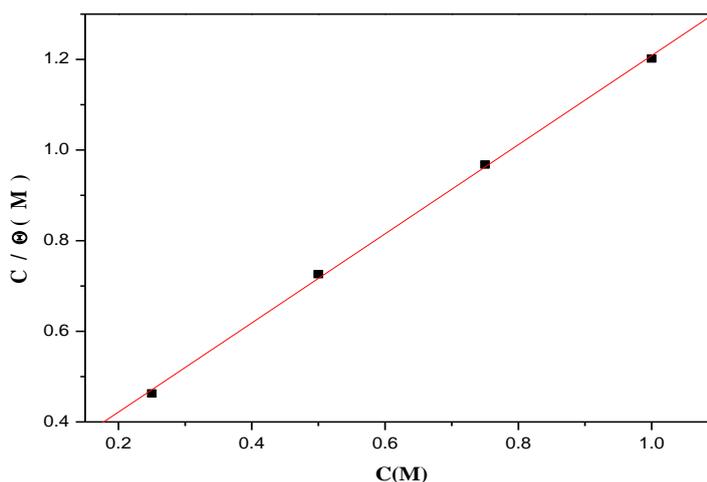


Figure 3. The relationship between C/θ and C in 0.5 M H₂SO₄

4. CONCLUSIONS

It can be concluded as follows:

- The pistachio essential oil (**PEO**) was found to perform in 0.5 M H₂SO₄.

- Polarization studies showed that the compounds under investigation were mixed type inhibitors.
- The inhibition efficiency of **PEO** increased with the concentration and reached a maximum at 1 g/l
- The weight loss, EIS, polarization curves, and linear polarization were in good agreement.
- Adsorption of inhibitor molecules on the C38 steel surface from 0.5 M H₂SO₄ followed the Langmuir isotherm.

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