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Valorization of polyphenols extracted from olive mill wastewater as ecological corrosion inhibitor on carbon steel in acid medium

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ABSTRACT

Our goal is to study the inhibition effect of polyphenols extracted from vegetable olives of a press system crushing unitonthe corrosion of carbon steelin HCl 1.0 M. The inhibition efficiency of polyphenols has been investigated by different methods, weight loss method, potentiodynamic polarization measurementsand electrochemical impedance spectroscopy (EIS).The effect of the temperature on the inhibition of acid hydrochloric corrosion of carbon steel by the addition of polyphenols was studied. Also the activation energy as other thermodynamic parameters for the inhibition process was calculated. The results obtainedconfirm that the polyphenols extracted from olive mill waste water collected from a press system acted as an efficient corrosion inhibitor as well as polyphenols from a three phase system. The inhibition efficiency increased with the inhibitor concentration but decreases with rise in temperature reaching a maximum of 94.4 % at a concentration of 1.5 (g/ L) of polyphenols.

Keywords: Olive mill waste water press, Polyphenols, Corrosion, inhibition, Carbon steel, HCl.

INTRODUCTION

Corrosion [1] is a surface phenomenon known as the attack of metals or alloys by their environment as air, water or soil in chemical or electrochemical reaction to form more stable compounds. It is necessary to devote more attention to metallic corrosion nowadays than earlier due to:

1. A more corrosive environment due to the increasing pollution of air and water.
2. An increased use of metals within all field of technology.
3. The use for special applications as in the atomic energy field of rare and expensive metals. The corrosion costs [2] in most of the countries are in the range of 2-4 % of the gross national product. So it is imperative that economically, useful measures should be taken to minimize corrosion.

The serious consequences of the corrosion process have become a problem of worldwide significance. The use of inhibitors is one of the most practical methods for protection against corrosion. The research in the field of ‘‘green’’ corrosion inhibitors has been directed toward the goal of using cheap, effective molecules of low or ‘‘zero’’ negative environmental impact [3]. Therefore, the use of non-toxic inhibitors has also become one of the major selection requirements, most organic inhibitors act by adsorption on the metal surface [4].

This phenomenon is influenced by the nature and surface charge of metal, type of aggressive medium and chemical structure of inhibitors. The adsorption of corrosion inhibitor depends mainly on physico-chemical properties of the molecule such as functional groups, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density of the donor atoms [5].

A study has already been done on the effect of polyphenols extracts from a three-system phases as an inhibitor of corrosion of carbon steel in a solution of 1.0 M HCl using weight loss and various methods [6].

In continuation of our program for the development of corrosion inhibitors with high effectiveness and efficiency, the present paper explore the use of polyphenols extracted from vegetable olives polyphenols as safe corrosion inhibitor for steel corrosion in hydrochloric acid solutions using gravimetric and potentiodynamic polarization techniques. The olive mill waste studied here was collected from a crushing unit works by a press system in the region of Meknes-Tafilalt of the Moroccan Picholine[7].

MATERIALS AND METHODS

The steel used in this study is a carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu, and the remainder iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600, and 1200), then rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water, and then dried at room temperature before use. The acid solutions (1.0 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with double-distilled water. The concentration range of polyphenols employed was 2–0.5 (g/L).

Extraction of polyphenols

An amount of 100 g of olive mill wastewater (OMW) filtered through a Whatman filter paper No. 1 was delipidated by 2x100 mL of hexan. The delipidated olive mill wastewater (OMW) were then extracted with 2x100 mL of ethyl acetate. The organic phase was dried over 3 g of anhydrous sodium sulfate and then concentrated using a rotary evaporator set at 60 ºC and a speed of 140 rev/min. This gave an overall yield of 1.367 ± 0.108 % [8].

Weight loss measurements

The steel sheets of 1,6×1,6×0,07 cm dimensions were abraded with different grades of emery papers, washed with distilled water, degreased with acetone and dried .After weighing accurately by a digital balance with high sensitivity the specimens were immersed in solution containing 1.0 M HCl solution with and without various concentrations of the investigated inhibitor. After the immersion period the steel specimens were washed with bidistilled water, degreased and dried and then weighed.

The measurements were carried out at the definite time interval of 6 h at room temperature using an analytical balance (precision ± 0.1 mg).

Electrochemical measurements

The electrochemical measurements were carried out using using **Voltalab PGZ 100** piloted by ordinate associated to "Volta Master 4" software. The corrosion cell used had three electrodes. The temperature was thermostatically controlled. The working electrode was carbon steel with the surface area of 1cm^2. A saturated calomel electrode (SCE) was used as a reference. All potentials are given with reference to this electrode. The counter electrode was a platinum plate of surface area of 1 cm^2.

A SCE was used as the reference and a platinum electrode was used as the counter electrode. All potentials are reported versus SCE. All electrochemical tests have been performed in aerated solutions at 308 K.

For polarization curves, the working electrode was immersed in the test solution for 30 min until a steady state open circuit potential (Eocp) was obtained. The scan rate was 1 mV/s started from an initial potential of -900 mV to -100 mV (vs SCE). Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mVs^{-1}. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potential after 30 min of exposure. All potentials were reported versus saturated calomel electrode (SCE). The impedance diagrams are given in the Nyquist representation. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit to give the intersections with the x-axis.

RESULTS AND DISCUSSION

Gravimetric study

Values of The inhibition efficiency η_{WL}(%) of the C-steel obtained from the weight loss measurements for different concentrations of polyphenols in 1 M HCl at 25 °C after 6 h of immersion are given in table 1. The corrosion rate (CR), inhibition efficiency η_{WL} (%)were calculated according to Eqs. (1)and (2) [9,10], respectively:

$$\varsigma = \frac{W}{St} \cdot 100 \quad (1)$$

$$\eta_{WL}\,(\%) = \frac{v0 - v}{v0} \times 100 \quad (2)$$

where **W** is the three-experiment average weight loss of the mild steel, S is the total surface area of the specimen, **t** is the immersion time and v_0 and **v** are values of the corrosion rate without and with addition of the inhibitor, respectively.

Table1; Corrosion rate of steel in 1M HCl with and without chamomile oil at various concentrations, and the corresponding inhibition efficiency

Inhibitor	Concentration (g/L)	V (mg.cm^{-2} /h)	η_{WL} (%)
Blank	0.0	1.070	-
	2.0	0.060	94.3
	1.5	0.053	95.04
polyphenols	1.0	0.120	88.78
	0.5	0.308	71,21

The analysis of the results of table 1, show that the polyphenols possesses interesting corrosion inhibition properties for C-steel studied in 1M HCl solution as mentioned by[11]. The variation of the inhibition efficiency **ηWL** (%)with inhibitor concentration is illustrated graphically in Figure 1 for 1.0 M HCl. It appears that the corrosion rate decreases,) while the inhibition efficiency **ηWL** (%) increases with increasing concentration of inhibitor reaching a maximum value of 95,04 at a concentration of 1,5 (g/L). The surface coverage increases with increasing the concentration of inhibitor. The results are likely due to the adsorption of natural compounds on the surface of the metal forming a molecular film layer or barrier between the metal and the corrosive medium according Obot [12]

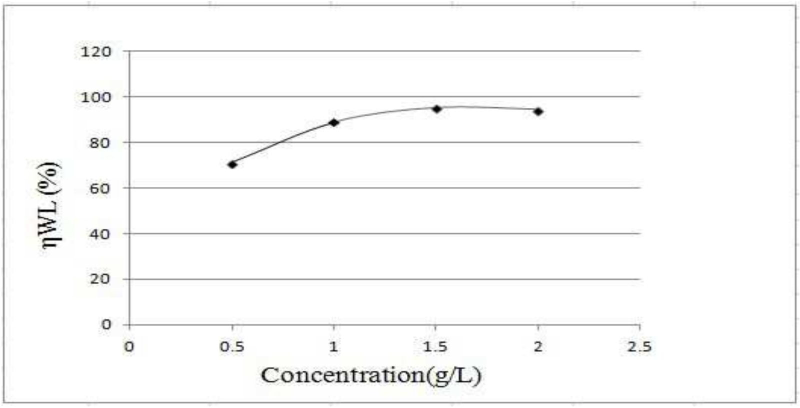

Figure 1: Variation of the inhibitive efficiency against the extract concentrations

Electrochemical impedance spectroscopy measurements

The corrosion behavior of steel, in acidic solution with and without polyphenols, is also investigated by electrochemical impedance spectroscopy (**EIS**) measurements Figure3.

It is clear to see that the impedance spectra are significantly changed with addition of different polyphenols concentration. The impedance spectra were measured at the corresponding open-circuit potentials. The capacitive loops Nyquist diagrams obtained are not centered on the real axis, due to the frequency dispersion, which can be connected to a surface, which generates a heterogeneous distribution frequency. This heterogeneity results from the roughness, impurities, and relocations of adsorption of the inhibitor and the formation of porous layer [13]. The impedance response of carbon steel in acid solution has significantly changed after adding the polyphenols, and the impedance of the inhibited system increased with inhibitor concentration. Moreover, the inhibitor concentration of polyphenols1,5(g/L) gives rise to a much larger semicircle diameter than the other four concentrations of polyphenols.

The electrochemical impedance spectra in complex plane presentation (Nyquist diagram) are characterized by one depressed semicircle, and the diameters of semicircle increases with the inhibitor concentration, in the presence of polyphenols. The same behavior is noticed in the case of uninhibited solution 1.0 M HCl.

The **EIS** results are simulated by, the simplest approach, the equivalent circuit shown in Figure2in which the ability of the double layer (**Cdl**) and the charge transfer resistance (**Rt**) are introduced in parallel, the resistance of the electrolytic solution (Rs) is inserted in series in the circuit.

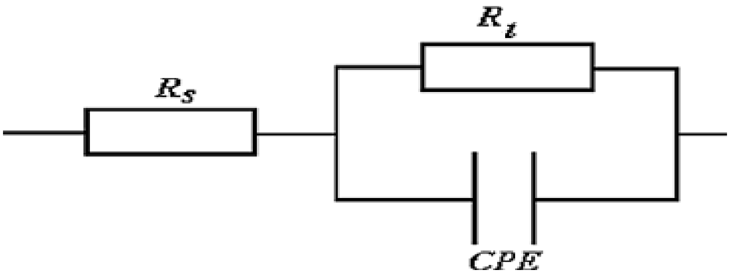

Figure 2: Electrical equivalent circuit used to fit the EIS data of the interface carbon steel/1.0 M HCl solution without and with polyphenols inhibitor

The double layer capacitance (**Cdl**) value is affected by imperfections of the surface, this effect is simulated through a constant phase element (CPE) [14] that is replaced with the capacitive element to give a more precise fit [15], the behavior observed from the Nyquist plot obtained for this inhibitor present is characteristic for solid electrodes and often referred to as frequency dispersion which is associate with to the surface heterogeneity[16]. The **CPE** impedance is given by [17, 18]:

$$Z_{CPE} = A^{-1}(iw)^{-n} \qquad (3)$$

Where A is the CPE constant, w is the angular frequency (in rad s^{-1}), $i^2 = -1$ is the imaginary number, and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface [18].

Depending on the value of n, CPE can represent
- Resistance (n = 0, A = R)
- Capacitance (n = 1, A = C)
- Inductance (n = - 1, A = L)
- Warburg impedance (n = 0.5, A = W).

In the ideal case of uniformity of active surface, the coefficient n is 1.

Considering that a **CPE** may be considered as a parallel combination of a pure capacitor and a resistor that is inversely proportional to the angular frequency, the value of capacitance, C_{dl}, can thus be calculated for a parallel circuit composed of a **CPE** and a resistor (R_t), according to the following equation:

$$C_{dl} = \frac{1}{2.\pi.f_m.R_t} \qquad (4)$$

With **Cdl**: double layer capacitance ($\mu F.cm^{-2}$); f max: maximum frequency (Hz) and **Rt**: Charge transfer resistance ($\Omega.cm^2$).

The electrochemical impedance parameters derived from these investigations are mentioned in Table 2.

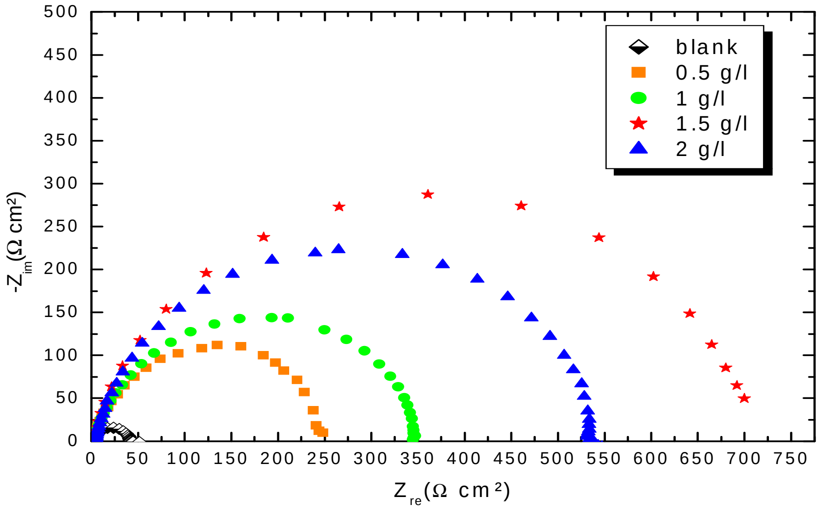

Figure3: Nyquist plots for carbon steel in 1.0 M HCl in the absence and presence of different concentrations of polyphenols at 308K

The inhibition efficiency got from the charge transfer resistance is calculated by:

$$\mathbf{IE\ \%} = \frac{(R_t - R^{o}_t)}{R_t} \times \mathbf{100} \qquad (5)$$

Were $\mathbf{R_t}$ and $\mathbf{R^0_t}$ are the charge transfer resistances in inhibited and uninhibited solutions respectively.

Table 2: Impedance parameters and inhibition efficiency values for carbon steel in 1.0 M HCl without and with different concentrations of polyphenols at 308 K

Concentration (g/L)	Rt ohm.cm²	CPEµF/cm²	n	IE%
blank	40	294	0.8	-
0.5	253	164	0.87	84
1	348	127	0.87	88.5
1.5	725	125	0.88	94.5
2	538	104	0.88	92.6

The analysis of the results from table 2 allows us to conclude that the transfer resistance values **(R_t)** are becoming more important as the polyphenols concentration increases. The inhibition efficiency **IE** (%) is evolving in the same way as the charge transfer resistance (**R_t**) and reaches a maximum value of 94.5%at a concentration of 1,5 (g/L).

When the concentration of the inhibitor increases, we notice that the size of the capacitive loop is increasing , which can be attributed to the process charge transfer, is well marked and that the value of the impedance obtained in without the addition of the inhibitor is lower than those obtained after adding it. This reflects the influence of the inhibitor on the process at the interface[19]. With the addition of the polyphenols, the capacitive nature of the double layer (**CPE**) decreases from294 for the blank, to 104for 2 (g/L)polyphenols this phenomenon is generally associated with the adsorption of organic molecules to the surface of the steel. In fact, plus inhibitor adsorbs more the thickness of the organic deposit increases and the capacity of the double layer decreases according to the expression given by the model Helmholtz of [20]:

$$C_{dl} = \frac{\varepsilon 0 \varepsilon}{\delta} S \qquad (6)$$

Where δ is the thickness of the protective layer, **S** is the electrode area, **ε0**the vacuum permittivity of vide and **ε** is dielectric constant of the medium.

On the other hand, the deviation parameter **n** has a tendency to decrease with the addition of inhibitor. The decrease in n may be connected with surface roughening which, due to the inhibitor molecules adsorbed on the metal surface, increases the heterogeneity [21], the values of **n** are close to **1** which means that the surface is not really heterogeneous.

Tafel polarization

Effect of concentration

Polarization curves of the carbon steel in 1.0 M HCl solutions without and with addition of different concentrations of polyphenols are shown in Figure 4.

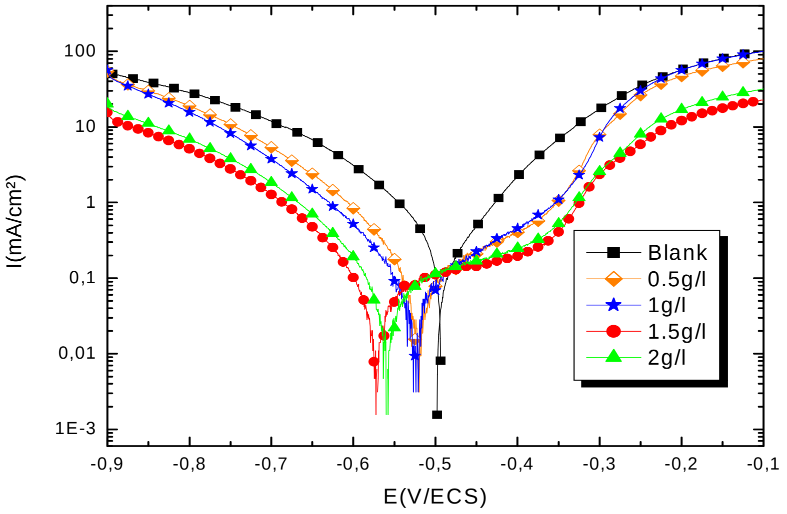

Figure 4:Potentiodynamic polarisation curves of steel in 1M HCl in the presence of different concentrations of polyphenol at 25°C

Various corrosion kinetics parameters including corrosion potential (E_{corr}), corrosion current density,(I_{corr}) anodic Tafel slop (b_a) and cathodic Tafel slope (b_c) were determined from these experiments by extrapolation method [22], are listed in Table3. The inhibition efficiency E (%) is defined as follows[23]:

$$E\% = \frac{I_{corr} - I_{corr\,(i)}}{I_{corr}} \times 100 \qquad (7)$$

Where I_{corr} and $I_{corr(i)}$ are the corrosion current densities for steel electrode in the uninhibited and inhibited solutions, respectively.

The cathodic branch represents the hydrogen evolution reaction, while the anodic branch represents the iron dissolution reaction Tafel extrapolation. The mechanism proposed for the corrosion of iron determines them and steel in acid solution is [24, 25]:

$Fe + A^{n-} \longrightarrow (FeA^{n+})_{ads}$
$(FeA^{n-})_{ads} \longrightarrow (FeA^{n-})_{ads} + ne^-$
$(FeA^{n-})_{ads} \longrightarrow (FeA^{n+})_{ads} + ne^-$
$(FeA^{n+})_{ads} \longrightarrow (Fe^{2+})_{ads} + A^{n-}$

The cathodic hydrogen evolution
$Fe + H^+ \longrightarrow (FeH^+)_{ads}$
$(FeH^+)_{ads} + ne^- \longrightarrow (FeH)_{ads}$
$(FeH^+)_{ads} + H^+ + ne^- \longrightarrow Fe + H_2$

Table3: Polarization data of carbon steel in 1.0 M HCl without and with addition of inhibitor at 25 °C

Concentration (g/L)	-Ecorr(mV/SCE)	Icorr (µA/cm²)	ba (mV/dec)	-b_c (mV/dec)	E%
Blank	498	467	210	94	--
0.5	525	79	206	82	83
1	522	54	192	83	88
1.5	579	26	180	80	94.4
2	560	42	150	82	91

In Table 3, the values of corrosion current density (**I_{corr}**) decreased while the inhibition efficiency increased with increasing the inhibitor concentration;this could be explained by the adsorption of the polyphenol on the Carbon

steel surface.Fig. 4 shows the negative shifting in corrosion potential (E_{corr}) of carbon steel, while the inhibitor strongly reduces both anodic and cathodic current density.
The potentiodynamic curves show that there is a clear reduction of both the anodic and cathodic currents in the presence of Polyphenols compared with those for the blank solution. The values of cathodic Tafel slope b_c in the presence of inhibitor was changing, which clearly indicates that this inhibitor influence the kinetics of hydrogen evolution reaction. This indicates an increase in the energy barrier for proton discharge leading to less gas evolution.It is observed that the cathodic reaction, hydrogen evolution,and the anodic reaction,dissolution metal, were inhibited; these results are unlike the ones found by Larif et al[11].The addition of the inhibitor reduces both the rate of cathodic and anodic reactions by reducing the current densities on both sides of the polarization curves in the potential region studied therefore reduces the corrosion rate.

The protection efficiency increases with C_{inh} reaching its maximum value, 94.4%, at 1,5(g/L),which indicates higher surface coverage of the metal and that Polyphenpls is a good inhibitor for Carbon steel in 1.0 M HCl.The results obtained from electrochemical are in good agreement with weight loss studies.

Effect of temperature

Effect of temperature on the corrosion behavior of C steel isinvestigated using polarizationmethods at the temperature in the range (298 – 328)K in the absence (Fig. 5) and the presence of polyphenol at 1.5 (g/L) (Fig. 6) in 1M HCl.

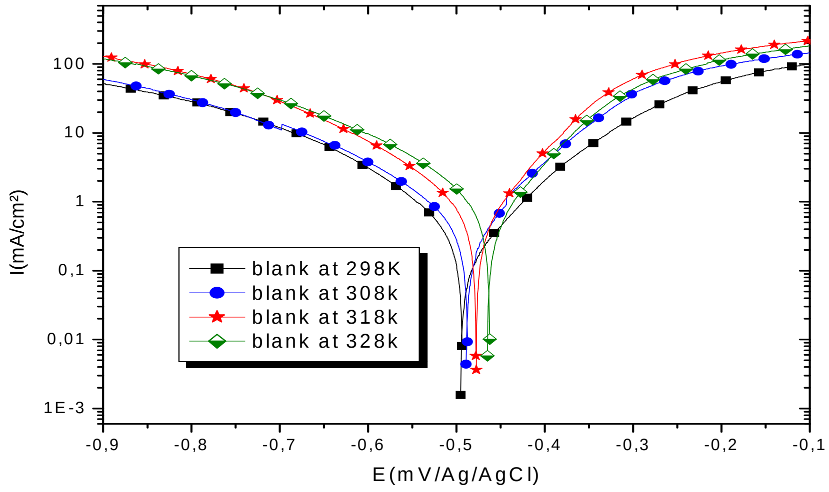

Figure 5:Potentiodynamic polarization curves of steel in 1M HCl at different temperatures

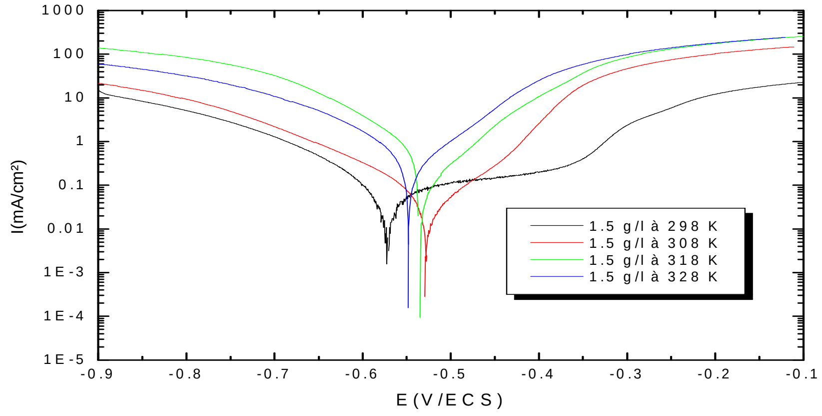

Figure6:Potentiodynamicpolarization curves of steel in 1M HCl in the presence of 1,5 (g/L) of polyphenols extract inhibitor at different temperatures

The values of the variation of corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c), and the degree of surface coverage (θ) with the concentration of inhibitor Polyphenols at all studiedtemperatures are given in Table 4. The surface coverage (θ) was calculated using:

$$\theta = \frac{E\,(\%)}{100} \qquad (8)$$

The inhibition efficiency E (%) is given by equation (7).

Table 4: Electrochemical parameters of steel in 1 M HCl at different temperatures in the absence and the presence of 1.5 (g/L) Polyphenols

Inhibitor	Temperature (K)	-Ecorr (mV/SCE)	Icorr (µA/cm²)	-bc (mV/dec)	E%	θ
Blank	298	498	467	170	-	-
	308	491	800	178	-	-
	318	475	1200	165	-	-
	328	465	1680	151	-	-
Polyphenols	298	579	26	80	94.43	0.944
	308	525	96	92	88.00	0.880
	318	535	125	82	89.58	0.895
	328	546	241	90	85.65	0.856

From these results, we note that an increase in temperature increases $\mathbf{I_{corr}}$, while the addition of Polyphenols decreases the $\mathbf{I_{corr}}$ values across the temperature range. The results also indicate that the inhibition efficiencies decreased with increasing the temperature. Such behavior can be interpreted due to the inhibitor acts by adsorbing onto the metal surface, leading to a decrease in the inhibition efficiency [26].

The activation energies (E_a) for the corrosion process in absence and presence of the extract are evaluated from Arrhenius equation [27]:

$$K = A \exp\left(\frac{-Ea}{RT}\right) \qquad (9)$$

Where**A** is the pre-exponential factor, **T** is absolute temperature, R the gas constant and **K** is the rate constant of metal dissolution reaction which is directly related to corrosion current density. Thus, the equation can be rewritten as [28]:

$$i_{corr} = A \exp\left(\frac{-Ea}{RT}\right) \qquad (10)$$

Where$\mathbf{i_{corr}}$ is the corrosion current density.This equation can be used to calculate the E_a values of the corrosion reaction without and with HE. Plotting the natural logarithm of the corrosion current density against**1/T**, the activation energy can be calculated from the slope.The temperature dependence of C-steel dissolution in 1 M HCl and in the presence inhibitor is presented in Figure 7.The values of activation energies are given in table 5.

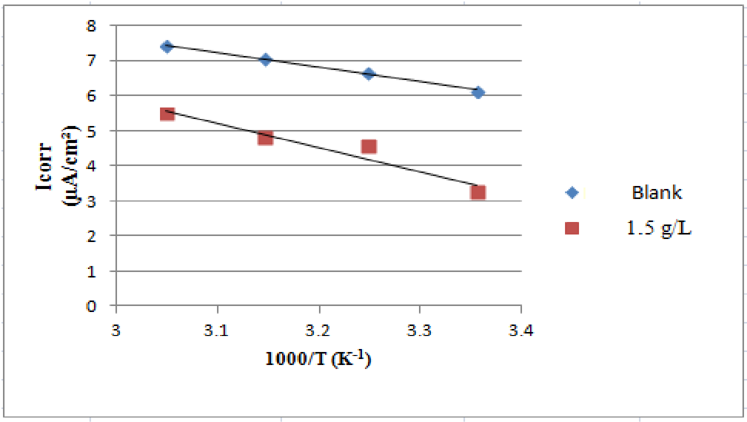

Figure 7:Arrhenius plots of C-steel in 1 M HCl with and without 1,5 (g/L) Po

Table 5: Calculated values of activation energies (Ea) for carbon steel in 1M HCl in absence and presence of 1,5 (g/L) of Polyphenols

	Ea (kJ/mol)	R^2
Blank	34.58	0.9938
1.5 (g/L) of Polyphenols	56.74	0.9309

The activation energy increased in the presence of Polyphenols, which indicated physical adsorption in the first stage [29]. The value of E_a found for Polyphenols is higher than that obtained for 1.M HCl solution. The increase in the activation energy was due to the corrosion reaction mechanism in which charge transfer was blocked by the adsorption of Polyphenols controlled by the surface reaction since the energy of the activation corrosion process in both the absence and presence of Polyphenols was greater than 20 kJ mol^{-1}[30].

CONCLUSION

The following conclusions are drawn from the study:

- The Results obtained qualified that the polyphenol tested is an efficient inhibitor.
- The inhibitor extracted from OMW Polyphenols has shown maximuminhibition efficiency 94.4% at 1.5 (g/L) concentration.
- Data obtained from weight loss measurements are in reasonably good agreement with those of the polarization studies.
- EIS measurement reveals that charge transfer resistance increases with increase in concentration of theextract, indicating that the inhibition increases with increase in concentration.
- Increase of temperature leads in a decrease of efficiency and an increase of the activation corrosion energy.

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