



## The study of the aqueous extract of leaves of *Pancreatium Foetidum Pom* as: Characterization of polyphenols, flavonoids, antioxidant activities and Eco-friendly corrosion inhibitor

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### Abstract

Antioxidant activity studied by using the DPPH radical trapping test. For this purpose, the phenols and flavonoids compounds were dosed. Quantitation of the phenolic and flavonoid compounds of the aqueous extract to the solvent (diethyl ether and ethyl acetate) was determined by spectrometry. Finally, the DPPH trapping activity of the extracts increased in the order of: diethyl ether fraction < ethyl acetate fraction < ascorbic acid. The inhibition of mild steel in the 1M hydrochloric acid solution is also studied. The aqueous extract of leaves of *Pancreatium Foetidum Pom*, was carried out by potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss studies. The results obtained show that the inhibition efficiency increases with the increase in inhibitor concentration and the variation in the inhibitory efficiency depends mainly on the type and nature of the substituents presents in the mixture (aqueous extract) to reach 98 % To 1 g / L.

### 1. Introduction

The family of Amaryllidaceae resembles a family of monocotyledonous plants. They include more than 800 species in 60 genus including Galanthus, Leucojum, Narcissus and Pancreatium. They are herbaceous plants, mainly bulbous, perennial, with deciduous leaves, and inferior ovary, they are suitable for temperate to tropical regions. Amaryllidaceae are herbaceous plants with an erect stem; the leaves often rectinerves, the flowers actinomorpha. The ovary is inferior (adherent); Sometimes a crown or paracorolle evolves from the perianth [1]. *Pancreatium foetidum Pom* belongs to Amaryllidaceae family, it's a plant endemic to north west of morocco and east of Alger according to Jahandiez and Maire [2].

Corrosion is the progressive destruction of a material due to its reaction with the environment, causing a slow, regular and irreversible deterioration of the metal. This major industrial problem has attracted many researchers in recent years. Before, it was known that the main strategy to prevent electrochemical corrosion is the isolation of metals from corrosive agents. Currently, the use of inhibitors is one of the most practical methods for corrosion protection. Considerable efforts have been made to find suitable compounds to be used as corrosion inhibitors in various corrosive media to stop or retard the corrosion of a metal. Recently, several studies have been carried out on the inhibition of corrosion of metals by synthetic organic molecules [3-7]. In spite of the high efficiency of

these synthesized organic compounds, they cause side effects on the environment, hence the need to replace them with biodegradable inhibitors, which are eco-compatible with the environment and which do not have side effects on the living being [8-11].

Several questions have arisen concerning the safety of chemicals, used in medicine or in the food industry under the action of oxygen free radicals which lead to changes in taste, odor, color and consequently to the loss of food quality and safety. So, it is essential to look for new effective and non-harmful antioxidant substances.

Despite the importance of oxygen in life, it can be toxic by itself and by the formation of free radicals, reactive oxygen species (ROS) which appear under the action of UV rays, radiation ionizing, numerous transition metals and thus during various enzymatic reactions. These ROS have numerous deleterious effects, causing premature aging, cardiovascular problems, atherosclerosis, diabetes and cancers [12]. Lipid oxidation is responsible for the formation of undesirable chemical compounds, resulting from unpleasant tastes and odors, reducing the quality of food [13]. Therefore, controlling oxidation is essential to manage the evolution of biological systems in their complexity, particularly in the case of foods whose degradation can have consequences for food safety [14]. To inhibit these unwanted processes, natural antioxidant additives are used [15-17]. The aim of the second part of this study is to evaluate the antioxidant activity of three bioactive substances (alkaloids, flavonoids and polyphenols) of the aqueous extract of leaves of *Pancratium Foetidum Pom*.

## 2. Experimental Section

### 2.1. Plant material

*Pancratium foetidum* plant was collected from Saïdia-Oujda, Morocco in May 2015. The plant was cleaned, dried and kept in dry place at the laboratory. The systematics of *PancratiumFoetidumPom* is as follow:

**Class:** Monocotyledons  
**Order:** Albumins  
**Family:** Amaryllidaceae  
**Genus:** *Pancratium*  
**Species:** *Foetidum*



**Figure 1:** Leaves of *Pancreatium foetidum Pom* (LPFP)

### 2.2. Aqueous extract

The aqueous extract of the leaves of *Pancreatium Foetidum* (LPFP) is obtained by a solid / liquid extraction by decoction.

- 100 g of leaves of *Pancreatium Foetidum* (LPFP) are placed in a boiling flask with 100 ml of water.
- Keep the mixture boiling for three hours in a soxhlet;
- At the end of the decoction, filter, recover and allow the solution to cool.

It is stated that the leaves of the studied plant are poor in essential oil. The reason why its aqueous extract was used.

### 2.3. Fractionating the aqueous extract [15, 17]

The mixture is extracted after filtration by two solvents of different polarity namely, ethyl acetate and diethyl ether, polarity indices respectively 0.58 and 0.38:

A sample of 100 ml of the extract recovered by steam distillation is hydrolyzed with 40 ml 2N HCl bath at 373 K for one hour, at the end of this treatment, plant debris clusters are formed and extract aqueous recovered is filtered and then mixed in a separating funnel and shaken thoroughly with diethyl ether or ethyl acetate. After settling in an ampoule, the upper organic phase is collected in an Erlenmeyer flask, the extraction is repeated 3 times with solvent renewal. The latter is due evaporated after drying the organic phase with anhydrous sodium sulfate, and the resulting extract is considered as the fraction of diethyl ether or ethyl acetate. The fractions thus obtained were stored in glass vials and then kept at a temperature of 277 to 278 K prior to analysis.

#### 2.4. Determination of total phenolics contents

Polyphenols are estimated by various methods such as the method of Prussian blue [18], but the most used is the Folin-Ciocalteu. This consists of a mixture of phosphotungstic acid ( $H_3PW_{12}O_{40}$ ) and phosphomolybdic acid ( $H_3PMO_{12}O_{40}$ ); it is reduced by the phenols in a mixture of the blue oxides of tungsten and molybdenum [19].

1 ml of Folin reagent (diluted 10 times in distilled water) was added to 200  $\mu$ l of sample or standard (gallic acid) with suitable dilutions in distilled water, after 4 min, 800  $\mu$ l of a solution sodium carbonate (75 mg / ml) are added to the reaction medium. After 45 minutes incubation at room temperature, the absorbance of the resulting solution is measured at 760nm. The same procedure was also applied to the standard solutions of gallic acid, and a standard curve was obtained. The concentrations of phenolic compounds expressed as  $\mu$ gallic acid equivalent per mg of extract were calculated according to the standard gallic acid graph.

All experiments were performed in triplicate assays, and gallic acid equivalent values were reported as X (average)  $\pm$  SD (standard deviation) of triplicates.

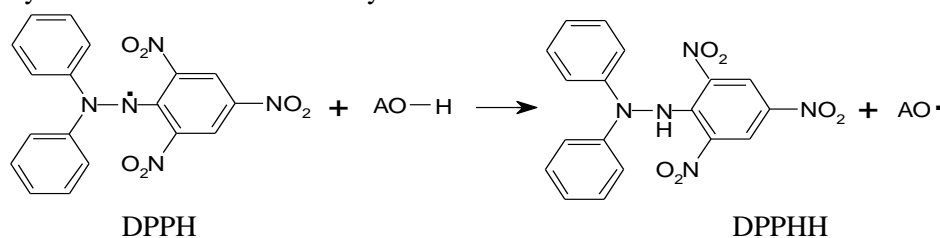
#### 2.5. Determination of total flavonoids contents

Quantification of flavonoids in extracts of leaves of *Pancreatium Foetidum* Pom were performed by the method of aluminum trichloride [20, 21].

1 ml of sample or standard (dissolved in methanol) was added to 1 ml of the solution of  $AlCl_3$  (2% in methanol). After 30 minutes of reaction, the absorbance is read at 415 nm. The concentrations of flavonoid compounds expressed as  $\mu$ grutin equivalent per mg of extract were calculated according to the standard rutin graph. All experiments were performed in triplicate assays and rutin equivalent values were reported as X  $\pm$  SD of triplicates.

#### 2.6. Antioxidant activity

We use 1,1-diphenyl-2-picrylhydrazyl (DPPH) to measure the free radical-scavenging activities of solvent extracts, as described by Hatano *et al.* [22]. The stable free radical DPPH (deep violet color) converts to 1,1-diphenyl-2-picrylhydrazine with discoloration by reaction with the antioxidants.



Where: (AO-H) represents a compound capable of yielding hydrogen to DPPH radical (violet) to transform it into picryldiphenyl hydrazine (yellow)[23].

The concentrations of the samples and standards studied are prepared in ethanol. Concentrations (between 0.2 and 2  $\mu$ g/ml) were added to 3.9 ml of a solution of DPPH radicals in ethanol.

The mixture was allowed to stand at room temperature for 30 minutes in the dark. The absorbance was measured at 517 nm against a blank. The radical-scavenging activity was expressed as percentage of inhibition (I%) according to the following formula [24]:

$$I (\%) = 100 * (A_{\text{control}} - A_{\text{sample}}) / A_{\text{control}}$$

Where  $A_{\text{control}}$  is the absorbance of the control reaction and  $A_{\text{sample}}$  is the absorbance of the test compound. The sample concentration providing 50% inhibition ( $IC_{50}$ ) was calculated from the graph of inhibition percentage against sample concentration. Tests were carried out in triplicate. Ascorbic acid was used as a positive control.

#### 2.7. Preparation of test specimens

The Mild Steel specimens tested in this present paper, are prepared with a composition (in% by weight) (0.21% C, 0.38% Si, 0.09% P, 0.01% Al, 0.05% Mn, 0.05% S).

The mild steel samples were prepared prior immersion in the tested solutions by polishing with SiC paper up to 1200 grade, washing with distilled water and then degreased with alcohol, washed again with distilled water then dried it by used filter papers. The electrolyte is a solution of HCl 1 mol / L, prepared using double distilled water.

### 2.8. Weight loss measurements

The gravimetric test is based on the immersion of the mild steel samples, in 100 ml of a 1M HCl solution containing the inhibitor (aqueous extract) at different concentrations, after be degreased, polished and weighed. Immersion is subjected to a temperature of 308 K to 6 hours.

Temperature corrosive environment is a factor that can affect the efficacy of inhibiting it. Given the importance of this factor, we performed tests of mass loss of steel in 1 M HCl with and without addition of the inhibitor at different temperatures between 318 and 348 K.

### 2.9. Electrochemical measurements

The corrosion cell involving three electrodes, mild steel as working electrode, saturated calomel electrode (SCE) as reference electrode and a platinum wire used as counter electrode. The exposed area of working electrode to solutions was  $1\text{Cm}^2$ .

The major electrochemical techniques used in this study are Tafel plots polarizations (TP) and Electrochemical impedance spectroscopy (EIS).

The polarization curves were recorded using a potentiostat type PGZ Volta Lab 301 to a scan rate of 1 mV/Sec. The electrode of steel was maintained at the corrosion potential for 30 minutes and the following pre-polarized -800 to -200 mV/SCE for 10 min, all experiments were repeated three times at the desired temperature of  $\pm 274$  K. Electrochemical impedance spectroscopy (EIS) was carried out with the same equipment used for the polarization measurements, leaving the frequency response analyzer out of consideration. Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mV/s. 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 was 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.

All electrochemical studies were carried out with immersion time of 1 hour, with different inhibitory concentrations of aqueous extract of leaves of *PancratiumFoetidumPom*, at 308 K.

Experiments are repeated three times to ensure the reproducibility.

## 3. ResultatsAnd Discussion

### 3.1. Total phenolic and flavonoid contents of solvent extracts

To determine the quantity of total phenols and flavonoids in the two fractions of aqueous extract of leaves of *Pancratium Foetidum Pom*, colorimetric methods (Folin-Ciocalteux and Aluminum Trichloride ( $\text{AlCl}_3$ ) are used).

**Table 1:** Determination of total polyphenols and flavonoids in both fractions extracts of leaves of *Pancratium Foetidum Pom*

	Extract	Polyphenols in $\mu\text{gequivalent of gallic acid per mg of extract}$	Flavonoids in $\mu\text{g equivalent of rutin per mg of extract}$
<i>Leaves of PancratiumFoetidumPom (LPFP)</i>	Fraction diethyl ether	14 $\pm$ 29	10 $\pm$ 0.2
	Fraction ethyl acetate	22 $\pm$ 25	17 $\pm$ 1.6

The content of total phenols estimated by the Folin-Ciocalteu method for each extract fraction was reported in  $\mu\text{g}$ gallic acid equivalent / mg of extract. The results show that ethyl acetate and diethyl ether fractions of aqueous extract of leaves of *Pancratium Foetidum Pom* have respectively moderate levels (22 $\pm$  25 and 14 $\pm$  29 $\mu\text{g}$  / mg equivalent gallic acid per mg of extract). The flavonoid content determined by the method trichloride aluminum of each extract fraction was reported in  $\mu\text{g}$  equivalent rutin / mg of extract. The results reveal that ethyl acetate and diethyl ether fractions of aqueous extract of leaves of *Pancratium Foetidum Pom* have respectively a small amount (17 $\pm$  1.6 and 10 $\pm$  0.2  $\mu\text{g}$  equivalent of rutin per mg of extract).

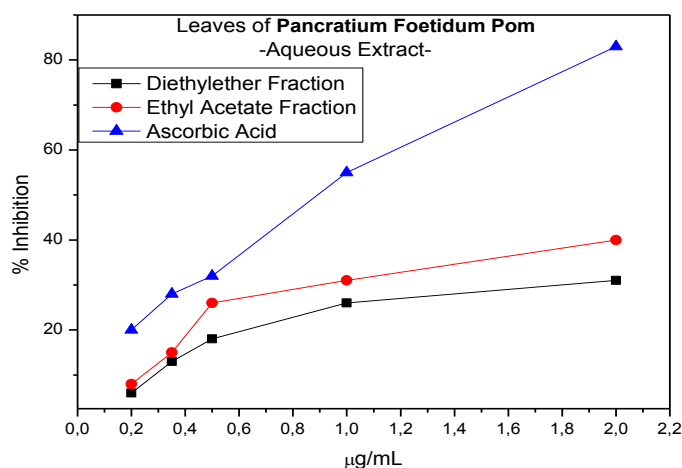
The determination of the quantity of the polyphenols and flavonoids in the two fractions of the aqueous extract of *Pancreatium Foetidum Pom*, showed that the aqueous extract studied has a low content of polyphenols and flavonoids.

### 3.2. Antioxidant Activity

Table 2 gives the results of free radical scavenging activity of fraction diethyl ether, fraction ethyl acetate and Acid Ascorbic (positive control). According to the findings, it is noted that the DPPH scavenging activities (%) were increased significantly with increasing the concentration of the studied samples from 0.2 to 2  $\mu\text{g/mL}$ .

**Table 2:**The antioxidant activity of the fractions (diethyl ether and ethyl acetate) of the aqueous extract of leaves of *Pancreatium Foetidum Pom* (LPFP) at different concentrations

Samples	Antioxidant Activities					
	Concentrations of the extract ( $\mu\text{g/ml}$ )	0.2	0.35	05	1	2
Diethylether fraction	Trapping Effect on DPPH (%)	6	13	18	26	31
	DPPH IC <sub>50</sub> ( $\mu\text{g/ml}$ )					
	Concentrations de l'extrait ( $\mu\text{g/ml}$ )	0.2	0.35	0.5	1	2
Ethyl acetate fraction	Trapping Effect on DPPH (%)	8	15	26	31	40
	DPPH IC <sub>50</sub> ( $\mu\text{g/ml}$ )					
	Concentrations ( $\mu\text{g/ml}$ )	0.2	0.35	0.5	1	2
Ascorbic acid	Trapping Effect on DPPH (%)	20	28	32	55	83
	DPPH IC <sub>50</sub> ( $\mu\text{g/ml}$ )					
	Concentrations ( $\mu\text{g/ml}$ )	0.2	0.35	0.5	1	2



**Figure 2:** Antioxidant power of two fractions of the aqueous extract of leaves of *Pancreatium Foetidum Pom*, (LPFP) OD reading after 30 min of incubation

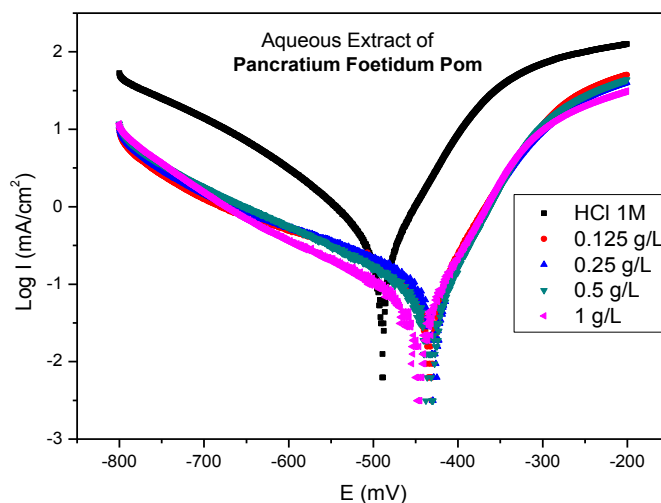
According to (table 2), the antioxidant activity of both fraction (ethyl acetate and diethyl ether) of aqueous extract, is much lower than ascorbic acid. Although, ethyl acetate fraction is slightly greater than the diethyl ether fraction (Figure 2). This activity of the aqueous extract increases with the concentration, this is explained by the fact that the studied samples give hydrogen to DPPH who then converted to the color violet in yellow and absorbs less light. When the concentration is high, more antioxidants DPPH is reduced, so less it absorbs light passing through it. We can explain the moderate antioxidant activity of both fraction of aqueous extract of *Pancreatium Foetidum Pom* leaves (LPFP), by the low content of polyphenols and flavonoids present in the aqueous extract of the plant studied. It is known that there is a relationship between the antioxidant activity and the content of

polyphenols and flavonoids [15, 17], which explains the moderate antioxidant activity exhibited by our aqueous extract. This low activity can also be explained by the presence of the total alkaloids in *PancreatiumFoetidumPom* [25]. The latter are known for their low antioxidant activities [26].

### 3.3. Potentiodynamic polarization curves

The potentiodynamic measurement results of mild steel in 1.0 M HCl solution without and with different range of inhibitor (aqueous extract of leaves of *PancreatiumFoetidumPom*) concentrations were shown in (Figure 3). The polarization parameters namely corrosion current density ( $I_{corr}$ ), corrosion potential ( $E_{corr}$ ), anodic Tafel slope ( $\beta_a$ ), cathodic Tafel slope ( $\beta_c$ ) and percentage inhibition efficiency ( $E_I$  %) were calculated from the Tafel curves and are given in Table 3. It can be observed that from Fig. 3, both the cathodic and anodic reactions were suppressed with the addition of inhibitor, which suggested that the inhibitor studied reduced anodic dissolution and also retarded the hydrogen evolution reaction [7].

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**Figure 3:** Tafel polarization curves in in HCl 1M with and without aqueous extract of leaves of *PancreatiumFoetidumPom*(LPFP) at different concentrations

The inhibition efficiency was evaluated from the measured  $I_{corr}$  values using the following relationship:

$$E_I(\%) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100$$

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

**Table 3:** The electrochemical parameters for mild steel in 1.0 M HCl solution without and with different concentration of aqueous extract of leaves of *PancreatiumFoetidumPom* (LPFP) at 308 K

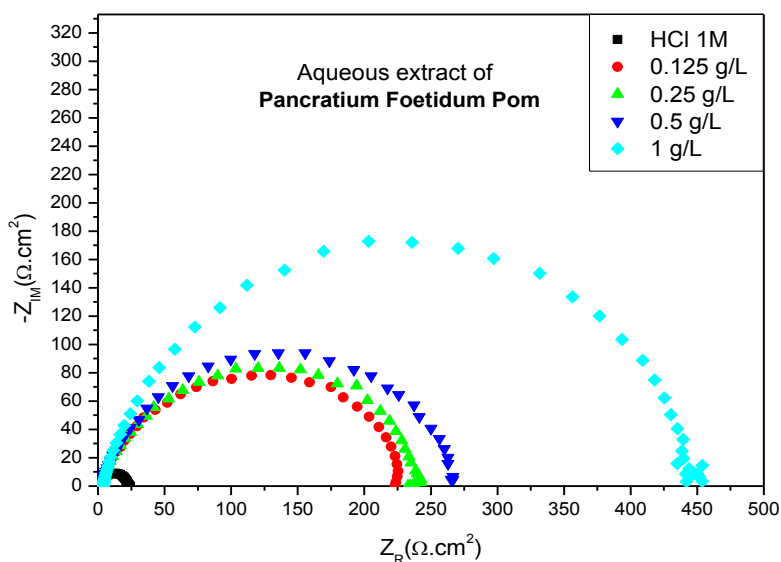
Inhibitor concentrations	$-E_{Corr}$ (mV)	$\beta_a$ (mV/dec)	$\beta_c$ (mV/dec)	$I_{Corr}$ (mA/cm <sup>2</sup> )	$E_I$ (%)
HCl 1M	490	74.8	-147.7	0.5779	-
0.125 g/L	433	55.7	-198.9	0.0678	88.27
0.25 g/L	428	51.7	-194	0.0638	88.96
0.5 g/L	428	48.3	-159.1	0.0427	92.61
1 g/L	447	52.3	-145.8	0.0279	<b>95.17</b>

The corrosion potentials ( $E_{\text{corr}}$ ) for the mild steel in the presence of aqueous extract are slightly shifted toward the positive potentials compared with the mild steel in 1.0 M HCl. Both anodic and cathodic current densities were reduced in the presence of inhibitor which suggests a mixed-type inhibitor behavior [27].

It is clear from (Table 3), that after increasing the concentration of inhibitor, the inhibition efficiency increased, while the corrosion current density decreased due to adsorption of inhibitor on the mild steel surface. The minor shift in  $E_{\text{corr}}$  value (62 mV) towards positive direction in the presence of inhibitor, as compared to the  $E_{\text{corr}}$  value in the absence of inhibitor indicates that aqueous extract of leaves of *Pancratium Foetidum* Pom (LPFP) act as mixed type inhibitor.

### 3.4. Electrochemical impedance spectroscopy studies

The Nyquist plots obtained from the EIS measurements for mild steel in 1.0 M HCl solutions at 308 K are shown in Fig. 4. The plots are characterized by a semicircle, which means the process was mainly controlled by capacitance and depressed semicircle reflects the surface in-homogeneity of structural or interfacial origin, such as those found in adsorption processes [28].



**Figure 4:** Nyquist plots recorded for mild steel in 1.0 M HCl solutions without and with different concentrations of aqueous extract of leaves of *Pancreatium Foetidum* Pom (LPFP)

The capacitive semicircle refers to the double layer capacitance and transfer resistance ( $R_{\text{ct}}$ ). The diameter of semicircle represents the value of transfer resistance ( $R_{\text{ct}}$ ) which indicates a decreasing trend in corrosion rate. The charge transfer resistance values ( $R_{\text{ct}}$ ) was calculated from the difference between impedance values at lower and higher frequencies as suggested by Haruyama et al. [29]. The double layer capacitance ( $C_{\text{dl}}$ ) was obtained from the following equation:

$$f(-Z_{\text{img}}) = \frac{1}{2\pi C_{\text{dl}} R_{\text{ct}}}$$

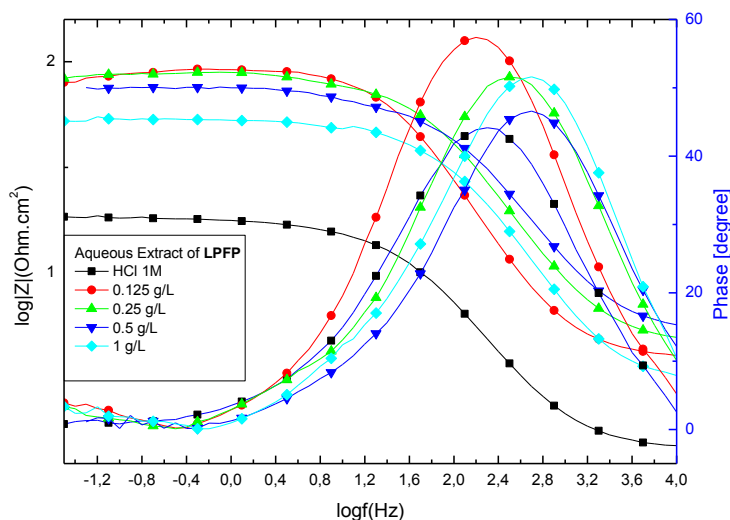
where  $Z_{\text{img}}$  is the frequency of maximum imaginary components of the impedance and  $R_{\text{ct}}$  is the charge transfer resistances.

The calculated electrochemical parameters of EIS measurements are listed in Table 4.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation:

$$E_{\text{Rp}}\% = ((R_{\text{ct}} - R_{\text{ct}}^0) / R_{\text{ct}}) \times 100$$

Where,  $R_{\text{ct}}$  and  $R_{\text{ct}}^0$  are the charge transfer resistance in absence and in presence of inhibitor, respectively.



**Figure 5:** The Bode and phase angle plots for mild steel in 1M HCl in the absence and presence of different concentrations of *LPFP* at 308 K, with an immersion time of 30min

**Table 4:** EIS parameters for the corrosion of mild steel in 1.0 M HCl containing aqueous extract of leaves of *Pancratium Foetidum* Pom at 308 K

Inhibitor concentration	$R_{ct}$ (Ohm.cm <sup>2</sup> )	$f_{max}$ (Hz)	$C_{dl}$ (μF/cm <sup>2</sup> )	$E_{Rp}$ (%)
HCl 1M	21.08	100	75.5	-
0.125 g/L	237.6	10	66.98	91.12
0.25 g/L	247.2	10	64.38	91.47
0.5 g/L	266.4	10	59.74	92.08
1 g/L	448.8	10	35.46	<u>95.3</u>

From the electrochemical impedance parameters and the inhibition efficiency ( $E_{Rp}$ %) which listed in Table 4, it is clear that the impedance spectra exhibit one single capacitive loop, indicating that the charge transfer takes place at the electrode/solution interface, the transfer process controls corrosion reaction and the presence of inhibitor does not change the mechanism of steel dissolution [30].

As the inhibitor concentration increased, the  $R_{ct}$  values increased and the  $C_{dl}$  values tended to decrease due to a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules acted by adsorption at the metal/solution interface. Addition of aqueous extract studied provided lower  $C_{dl}$  values, probably because of replacement of water molecules by inhibitor molecule at the electrode surface. In addition, the inhibitor molecules may reduce the capacitance by increasing the double layer thickness according to the Helmholtz model:

$$\delta_{org} = \frac{\epsilon_0 \epsilon A}{C_{dl}}$$

where  $\epsilon$  is the dielectric constant of the medium,  $\epsilon_0$  is the vacuum permittivity, A is the electrode surface area and  $\delta_{org}$  is the thickness of the protective layer.

The data in Table 4 reveal that the values of inhibition efficiency obtained by EIS are comparable to those obtained by potentiodynamic measurement.



Figure 5 illustrates the Bode and phase angle plots for mild steel in 1M HCl in the absence and presence of different concentrations of inhibitor studied at 308 K, with an immersion time of 30min. When analyzing the Nyquist diagrams, it seems that these curves consist of a depressed capacitive loop semicircle with one capacitive time constant in Bode-phase plots for all compounds study.

### 3.5. Weight loss study

#### 3.5.1. Effect of inhibitor concentration

Table 5 shows the results obtained from weight loss measurements for mild steel in 1.0 M HCl solutions in the absence and presence of different concentrations of aqueous extract of *Pancratium Foetidum Pom*. We observe from the results, that the E% of aqueous extract increases from 92.57% to 98.01% with the increase in inhibitor concentration from 0.125 to 1 g/L. Indeed, corrosion rate values of mild steel decreases from 0.32 to 0.0063 mg/cm<sup>2</sup>.h. The increase in efficiency may be due to the blocking effect of the surface by adsorption, film formation mechanisms and can be attributed to the increase of the covered surface ( $\theta$ ) which decreases the effective area of corrosion attack [31]. The results confirm that the aqueous extract of leaves of *Pancratium Foetidum Pom* is an efficient corrosion inhibitor. The high efficiency is probably due to the synergistic or antagonistic effects of the various constituents of the aqueous extract studied.

**Table 5:** Weight loss values of various concentrations of aqueous extract of leaves of *Pancratium Foetidum Pom* (LPFP) at 308 K in 1.0 M HCl solution

Concentrations	C <sub>R</sub> (mg/cm <sup>2</sup> .h)	$\theta$	E %
HCl (1M)	0.32	----	----
0.125 g/L	0.0237	0.92	92.57
0.25 g/L	0.0204	0.93	93.62
0.5 g/L	0.0162	0.94	94.93
1 g/L	0.0063	0.98	98.01

### 3.6. Influence of Temperature

The study of the influence of temperature on the rate of corrosion inhibition of mild steel by our inhibitor (aqueous extract of leaves of *Pancratium Foetidum Pom*) was performed at temperatures 318, 328, 338 and 348 K in the absence and in the presence of inhibitor at 1g/L, to determine the activation energies, enthalpies and entropies of activation of the corrosion process and thus provides information on the mechanism of inhibition. The corresponding data are shown in table 6. The comparative study of table 6 showed that the corrosion rate increases with increase in temperature in both the inhibited solutions and uninhibited, while the efficiency of inhibiting (aqueous extract of leaves of *Pancratium Foetidum Pom*) product decreases slightly. A decrease in the efficiency of inhibition with increasing temperature in the presence of our compound may be due to the weakening of physical adsorption.

**Table 6:** Various corrosion parameters for steel in 1.0 M HCl in absence and presence of optimum concentration of aqueous extract of leaves of *Pancratium Foetidum Pom* (LPFP) at different temperatures

Temperature (K)	Inhibitor	CR(mg/cm <sup>2</sup> .h)	E (%)
318	HCl 1M	2.0649	-
	Aqueous Extract	0.1519	<b>92.64</b>
328	HCl 1M	4.0689	-
	Aqueous Extract	0.426	<b>89.53</b>
338	HCl 1M	6.9998	-
	Aqueous Extract	0.8889	<b>87.3</b>
348	HCl 1M	9.7914	-
	Aqueous Extract	1.4765	<b>84.92</b>

To determine the  $E_a$ , we use the Arrhenius equation:

$$C_R = A \exp\left(-\frac{E_a}{RT}\right)$$

It's used to account for the effect of temperature ( $T$ ) on the corrosion rate ( $C_R$ ), the change in the log of corrosion rate as a function of the reciprocal of the absolute temperature is a linear function of  $T^{-1}$ . The corresponding relation provides access to the activation energies:

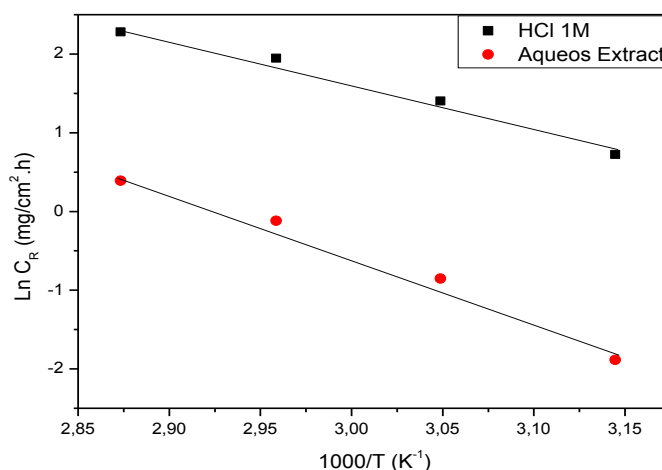
$$\ln C_R = -\frac{E_a}{RT} + \ln A$$

To access the activation thermodynamic characteristics, enthalpy ( $\Delta H_a$ ) and entropy of activation ( $\Delta S_a$ ), we used the Arrhenius equation transition [32]:

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right)$$

where  $C_R$  is the corrosion rate,  $R$  the gas constant,  $T$  the absolute temperature,  $A$  the pre-exponential factor,  $h$  the Planck's constant and  $N$  is Avogadro's number,  $E_a$  the activation energy for corrosion process,  $\Delta H_a$  the enthalpy of activation and  $\Delta S_a$  the entropy of activation.

The curves of variation of the logarithm of the corrosion rate as a function of the reciprocal of the absolute temperature ( $T^{-1}$ ) is recorded in (Figure 6). That the curves obtained in the form of lines.

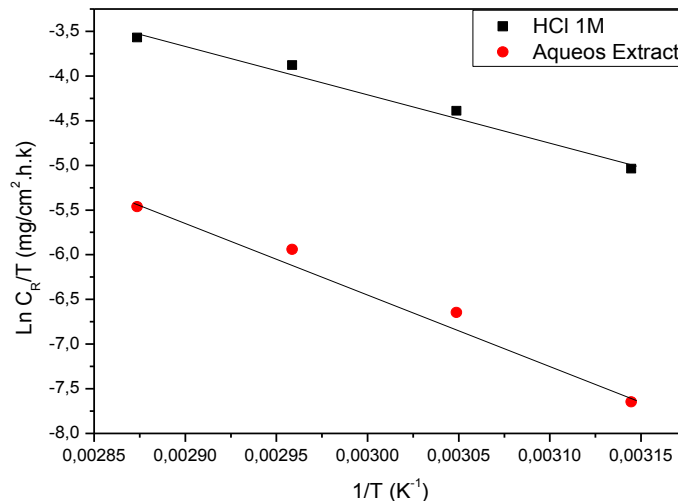


**Figure 6:** Arrhenius plots of  $\ln C_R$  vs.  $1/T$  for steel in 1.0 M HCl in the absence and the presence of (*Aqueous leaves Extract*) at optimum concentration

Figure 7 shows the variation of  $\ln(C_R/T)$  function ( $1/T$ ) as a straight line with a slope of  $(-\Delta H_a/R)$  and the intersection with the y-axis is  $[\ln(R/Nh) + (\Delta S_a/R)]$ . From these relationships, values of  $\Delta S_a$  and  $\Delta H_a$  can be calculated. The activation parameters ( $E_a$ ,  $\Delta H_a$  and  $\Delta S_a$ ) calculated from the slopes of Arrhenius lines in the absence and presence of our inhibitor are summarized in table 7.

It is clear from table 7 that the value of the apparent activation energy for the inhibited solution was higher (69.81 kJ/mol) than that for the uninhibited solution (48.13 kJ/mol), indicating that the dissolution of mild steel was decreased due to formation of a barrier by the adsorption of the inhibitors on metal surface [7].

The values of  $E_a$  and  $\Delta H_a$  were increased in the presence of inhibitor, suggesting that the energy barrier of the corrosion reaction increases, meaning that the dissolution of the steel is difficult [33]. According Gomma et al [34], the activation energy is much higher than the inhibitor is more effective. However, the positive sign of the endothermic enthalpy reflects the nature of the dissolution of the steel. We note that the variation of the activation energy  $E_a$  and the enthalpy of  $\Delta H_a$  vary in the same way with the concentration of inhibitor, which satisfies the relationship between  $E_a$  and thermodynamics as  $\Delta H_a$ :  $E_a - \Delta H_a = RT$  [35].



**Figure 7:** Arrhenius plots of  $\text{Ln}(C_R/T)$  vs.  $1/T$  for steel in 1.0 M HCl in the absence and the presence of (Aqueous extract) at optimum concentration

**Table 7:** Activation parameters for the steel dissolution in 1.0 M HCl in the absence and the presence of (aqueous of leaves extract) at 1g/L

Inhibitor	$E_a$ (kJ/mol)	$\Delta H_a^\circ$ (kJ/mol)	$\Delta S_a^\circ$ (J/mol. K)	$E_a - \Delta H_a$ (KJ/mol)
HCl 1M	48.13	45.36	-96.27	2.77
Aqueous Extract	69.81	67.05	-49.37	2.76

The value of  $\Delta S_a$  was lower for the uninhibited solution than that for the solution with inhibitor. This might be attributed to the rate-determining step for the activated complex was the association rather than the dissociation step [36]. As seen from Table 7, the shift of  $\Delta S_a$  to more positive values in the presence of the inhibitor, thus the increase in disorder, is a driving force that can overcome the barriers for the adsorption of inhibitor onto the metal surface.

## Conclusion

The following remarks can be made:

- There is a relationship between the total polyphenol, flavonoid content and antioxidant activity.
- Aqueous extract of *Pancreatium Foetidum* Pom leaves (LPFP), has a moderate antioxidant activity.
- Tafel polarization measurements indicate that the aqueous extract of leaves of *Pancreatium Foetidum* Pom (LPFP) act essentially as a mixed type inhibitor.
- The increase in the charge transfer resistance and decrease in double layer capacitance values, with the increase in the inhibitor concentration, showed that the aqueous extract of *Pancreatium Foetidum* Pom formed protective layers on the mild steel surface, covering areas where HCl solution degrades and corrodes rapidly.
- Inhibition efficiency increases with increase in the concentration of aqueous extract but decreases slightly with rise in temperature.
- Results obtained through weight loss measurements and electrochemical tests demonstrated that the aqueous extract of leaves of *Pancreatium Foetidum* Pom act as efficient corrosion inhibitor of the mild steel in 1 M HCl solution.
- Several authors have shown great interest in corrosion by using plant extracts (extracts and essential oils) as corrosion inhibitors in HCl medium, the added value of our work is that we obtained a very high efficiency using a very low concentration (0.125 g / L  $\rightarrow$  92.57%) of the extract studied.

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