

Cistus monspeliensis extract as antioxidant and corrosion inhibitor of ordinary steel in 1 M hydrochloric acid medium

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Abstract: The aim of this study is the valorization of the *Cistus monspeliensis* plant, native to North of Morocco, as antioxidant and corrosion inhibitor. Firstly, the plant is extracted by maceration in a mixture of water/acetone solvents. Phytochemical tests are carried out on the extract obtained. The antioxidant power of *Cistus monspeliensis* extract is evaluated by two methods: the test of reduction of the free radical DPPH[•] (1,1-diphenyl-2-picryl hydrazyl) and that of Ferric reducing antioxidant power (FRAP). The electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization are used to study the anticorrosion effect of *Cistus monspeliensis* extract. The results showed that the extract, 27.6% yield, contains phenolic compounds in the form of flavonoids, hydrolysable and condensed tannins, saponins, reducing sugars and glycosides. This extract has an antioxidant capacity similar to that of ascorbic acid with an inhibition concentration of 0.077 mg/mL 0.102 mg/mL for DPPH and FRAP test, respectively. Tafel plots show that the extract is an excellent cathodic inhibitor. The maximum inhibition efficiency of 92 % was obtained with 0.25 g/L of the inhibitor at 298 K. The impedance plot is characterized by a single capacitive loop attributed to the charge transfer process. The results also showed that the inhibitor acts on the surface of the metal principally by adsorption, leading to the formation of a protective film limiting the corrosion of ordinary steel.

Keywords: *Cistus monspeliensis*; antioxidant power; corrosion inhibitor; DPPH; FRAP; ordinary steel.

1. Introduction

Acid pickling of surfaces is one of the industrial processes used for the removal of scales. One of the severe problems associated with the use of acids is the corrosion of metallic substrates. For that, synthetic inhibitors have been used to overcome this problem ¹. However, most of these inhibitors are toxic ^{2,3}. Therefore, ecological inhibitors, based on plant extracts, of a non-toxic nature are suitable candidates for replacing synthetic inhibitors because of their abundant sources and low cost ⁴⁻⁷. Indeed, the ability of these inhibitors is generally attributed to the presence of secondary metabolites (polyphenols, alkaloids, saponins, etc.) having antioxidant power, readily available and renewable ^{8,9}. Currently, natural inhibitors are a topic of research in development based on the number of publications coming out each year ¹⁰⁻¹⁴. The tests carried out on the study of

anticorrosive properties of plant extracts gave promising results ¹⁵⁻¹⁷. Hence, Table 1 represents certain previous studies on the corrosion inhibition of steel in 1 M HCl medium by green inhibitors, using polarization tests and electrochemical impedance spectroscopy.

The natural plant products are also used as natural antioxidants to replace the synthetic antioxidants, which have toxic and dangerous effects ²⁵. It has been suggested that some plants, which have antioxidant activity, could decrease the risk of disease linked to oxidative stress in humans, thanks to the improvement of its antioxidant defence system, inhibition of the production of reactive oxygenated species and also to the redox properties of antioxidants ²⁶⁻²⁸. There is a large variety of methods to determine this activity (DPPH, FRAP, CUPRAC, ORAC, ABTS, beta-carotene, etc.). Most are spectrophotometric methods

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based on the coloring or discoloration of a reagent in the reaction medium. The best results are often obtained by the combination of several methods²⁹⁻³².

Table 1. List of plant extracts used as corrosion inhibitors on corrosion of steel in acidic medium.

Name of inhibitor	Metal	Electrolyte	Efficiency
Chinese gooseberry fruit shell extract ¹⁸	Mild steel	1M HCl solution	92%
<i>Rosa canina</i> fruit extract ¹⁹	Mild steel	1M HCl solution	86%
<i>Ammi visnaga</i> L. Lam Seeds extract ¹⁷	Mild steel	1M HCl medium	84%
Hydro-alcoholic extract of used coffee grounds ²⁰	C38 steel	1M HCl medium	97.36%
<i>Zingiber officinale</i> rhizomes essential oil ²¹	Ordinary steel	1M HCl solution	96%
<i>Acacia concinna</i> Pod extract ²²	Mild steel	0.5 M sulphuric acid	94%
Orange zest essential oil ²³	Mild steel	1 M HCl medium	75.64%
<i>Cinnamomum zeylanicum</i> extract ²⁴	Carbon steel	1M HCl solution	81.1%

The genus *Cistus* includes species of medicinal plants with various biological properties^{9,33-36}. The therapeutic properties of the species *Cistus monspeliensis* have been demonstrated in vitro; they are due to the presence of active compounds such as polyphenols^{33,37,38}. These phenolic compounds are essential for human nutrition and are of considerable interest because of their antioxidant properties^{39,40}. *Cistus monspeliensis* is a shrub of the Cistaceae family, which usually grows around the Mediterranean. In Morocco, it grows in different regions, particularly in northern Morocco (Rif region) on dry and sunny soils where it blooms in spring. The plant is a very fragrant, greenish shrub with sessile leaves, sticky, coarsely reticulated, with rolled edges; it has very fragrant white flowers 2 to 3 cm long⁴¹. This Moroccan medicinal plant is known locally as "shtapa" is traditionally used for the treatment of diabetes disease and to fight against insects^{33,42,43}.

To our knowledge, *Cistus monspeliensis* has never been studied for corrosion inhibition of ordinary steel in hydrochloric acid. The present study investigates the antioxidant activity of the *Cistus monspeliensis* extract using free radical DPPH (1,1-diphenyl-2-picryl hydrazyl) reducing capacity and the ferric reducing antioxidant power (FRAP), and examines its inhibition action on corrosion, of ordinary steel in 1M HCl solution, by electrochemical methods such as potentiodynamic polarization and electrochemical impedance spectroscopy.

2. Materials and methods

2.1. Preparation of *Cistus monspeliensis* extract

Firstly, the aerial part of dried *Cistus monspeliensis* was ground and extracted using the Soxhlet apparatus in hexane for 2 hours. The residue of the extraction is then extracted by maceration in an acetone/water mixture (70/30, v / v) for 2 hours. The mixture was then filtered, concentrated on evaporating the solvents and lyophilized.

2.2. Phytochemical tests

The phytochemical tests are used to search for the different families of chemical compounds present in the plant by well-known qualitative reactions. The detection of these chemical compounds is based on precipitation reactions, a specific color change, or examination under ultraviolet light. The tannins are detected using a ferric chloride solution (FeCl₃, 2%). The presence of flavonoids is obtained by the reaction of the plant extract with concentrated hydrochloric acid and magnesium turnings. The presence of alkaloids is indicated by the appearance of an orange precipitate in the presence of the Dragendorff's reagent. Saponins are characterized by the presence of foam. The detection of the reducing compounds consists of treating the extract with Fehling liquor and then heating it in a water bath; a positive test is indicated by the formation of a red brick precipitate. Besides, to test the presence of glycosides, the reaction consists in adding to the solution of the extract acetic acid, concentrated sulfuric acid and drops of FeCl₃ at 2%⁴⁴⁻⁵⁰.

2.3. Study of the antioxidant activity

The antioxidant activity of *Cistus monspeliensis* extract was determined by two methods: the DPPH free radical reduction test (1,1- diphenyl-2-picryl hydrazyl) and Ferric Reducing Antioxidant Power (FRAP).

2.3.1. DPPH free radical reduction test

In this test, the reducing power of *Cistus monspeliensis* extract was measured according to the protocol described by Olugbami et al.⁵¹ with some modification. A solution of 76 µM DPPH in ethanol is prepared, and 2 mL of this solution is added to 0.1 mL of each extract solution. A blank is prepared in parallel with methanol. The whole is then incubated in the dark at room temperature for 30 minutes. The absorbance of the mixture is measured at 517 nm. The antioxidant activity of the extract is compared to that

of ascorbic acid. The percentage inhibition is calculated according to this formula:

$$\% \text{ inhib} = \frac{(\text{Abs}_{\text{blank}} - \text{Abs}_{\text{sample}})}{\text{Abs}_{\text{blank}}} \times 100$$

Where $\text{Abs}_{\text{blank}}$: absorbance of the blank, $\text{Abs}_{\text{sample}}$: absorbance of the sample.

This formula allowed to trace the straight line ($y = ax + b$) representing the variation of the percentage inhibition of each sample. From this regression equation, it is possible to calculate the concentration that reduces 50% of DPPH in each sample and ascorbic acid. This concentration, termed as IC_{50} , is usually calculated by the following equation:

$$\text{IC}_{50} = (50 - b)/a$$

Where a: slope of the line, b: intercept of the line

2.3.2. Ferric Reducing Antioxidant Power FRAP

The ferric reducing antioxidant power (FRAP) of *Cistus monspeliensis* extract was evaluated following the method described by Gonçalves et al.⁵². In test tubes each containing 1 mL of the sample solution, 2.5 mL of phosphate buffer (0.2 M, pH 6.6) and

2.5 mL of potassium hexacyanoferrate [$(\text{K}_3\text{Fe}(\text{CN})_6$, 1%)] were added. The mixture was incubated at 50°C for 20 minutes. 2.5 mL of 10% trichloroacetic acid was then added, and the mixture was centrifuged at 3000 rpm for 10 minutes. Finally, 2.5 mL of supernatant, 2.5 mL of distilled water were mixed with 0.5 mL of ferric chloride [(FeCl_3) , 0.1%] are added. A blank is prepared under the same operational conditions. The reading of the optical density is performed at 700 nm, three measurements are determined for each solution. The antioxidant power of the extracts is evaluated by comparing curves obtained with the straight line of the ascorbic acid used as standard. The results are obtained by calculating IC_{50} , which expresses the concentration equivalent to the absorbance 0.5⁵³.

2.4. Specimen preparation

The material used, as the working electrode for polarization and EIS measurements, in this study is ordinary steel, its chemical and mass composition are illustrated in Table 2. Coupons were mechanically cut into 1×1 cm, polished with emery paper (from 120 to 2000 grade), rinsed by distilled water and dried at room temperature before each test.

Table 2. Weight and chemical composition of the material used.

Element	C	Si	Mn	Cr	Mo	Ni	Al	Cu	Co	V	W	Fe
%	0.11	0.24	0.47	0.12	0.02	0.1	0.03	0.14	<0.0012	<0.003	0.06	Balance

2.5. Solution preparation

The corrosive solution used in this study was an acid solution (1 M HCl), obtained by dilution of concentrated hydrochloric acid (37%) with distilled water. The concentration range of *Cistus monspeliensis* extract studied was varied from 0.05 to 1 g/L.

2.6. Electrochemical tests

Electrochemical tests including potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) were performed using a three-electrode cell: Platinum foil, saturated calomel electrode (SCE) and ordinary steel strips as a counter, reference and working electrodes, respectively. All experiments were recorded using PGZ 100 Potentiostat/ Galvanostat controlled by a computer associated with "Volta Master 4" software that was used for evaluating the experimental data. Electrochemical experiments were analyzed using electrochemical software ORIGIN 6. Electrochemical parameters were then extracted using to EC-Lab V10.02 software.

2.6.1. Polarization measurements

Polarization measurements were carried out using a three-electrode cell: platinum as a counter electrode, ordinary steel as a working electrode, and a saturated calomel electrode (SCE) as the reference electrode. A mixture of 50 mL HCl (as blank) and different

concentrations of the extract were used as test solutions for this study. Before any tests, the electrochemical system was stabilized for 30 minutes to attain steady-state corrosion potential (E_{corr}). The anodic and cathodic polarization curves were recorded by a constant sweep rate of 1 mV/s. Corrosion current density (i_{corr}) and corrosion potential (E_{corr}) values were obtained by software, and inhibition efficiency (η_{pp}) at different inhibitor concentrations was calculated using the following equation⁵⁴:

$$\eta_{\text{pp}} = \left[\frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \right] \times 100$$

Where i_{corr}^0 and i_{corr} are the corrosion current densities of ordinary steel in the absence and presence of inhibitor, respectively.

2.6.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy experiments were carried out under the same conditions as the plot of polarization curves, with a frequency range from 100 kHz to 100 MHz using (peak to peak) alternating amplitude signals of 10 mV. The EIS diagrams were plotted in the Nyquist representation. From these plots, the charge transfer resistance (R_{ct}) and the double-layer capacitance (C_{dl}) values were investigated, and inhibition efficiency (η_{imp}) was calculated at each inhibitor concentration using the following equation⁵⁵:

$$\eta_{\text{imp}} = [(R_{\text{ct}} - R_{\text{ct}}^0)/R_{\text{ct}}] \times 100$$

Where R_{ct} and R_{ct}^0 are the charge transfer resistance values of ordinary steel in the presence and absence of inhibitor, respectively.

3. Results and discussion

3.1. The yield of extraction and phytochemical tests

After delipidation by hexane, *Cistus monspeliensis* extraction by maceration in an acetone/water mixture gave a 27.6% yield of polar extract. In addition, the

phytochemical characterization tests carried out on the extract obtained provided the results illustrated in Table 3. These results show that this extract is rich on phenolic compounds in the form of hydrolysable tannins, condensed tannins and flavonoids; it also contains sugars and glycosides. In previous work, Karim et al. ⁵⁶ reported that the aqueous extract of Moroccan *Cistus monspeliensis* is obtained with a yield of 18.83%. Another study showed that the yield of the ethanolic extract of the same plant from north-west Morocco is 25.18% ⁵⁷.

Table 3. Results of phytochemical tests carried out on the various extracts.

	Hydrolysable tannins	Condensed tannins	Flavonoids	Alkaloids	Saponins	Reducing sugars	Glycosides
Extract	+	+	+	-	+	+	+

3.2. Result of antioxidant activity

The straight lines in Figure 1 represent the variation, as a function of the concentration of the extract, of the absorbance obtained in the FRAP test (A) and the percentage of inhibition obtained in the DPPH reduction test (B). In the same figure, these lines are compared with those obtained with ascorbic acid, the reference antioxidant. Table 4 shows the $IC_{0.5}$ and IC_{50} values obtained respectively in the FRAP and DPPH test for the extract and ascorbic acid. The extract showed a very high ability to reduce ferric ion with an $IC_{0.5}$ value of 0.102 ± 0.006 mg/mL, which is close to that of ascorbic acid at 0.093 ± 0.003 mg/mL for the

test FRAP. This reducing power can be attributed to the presence of phenolic compounds; previous studies showed a good correlation between the reducing power of iron and the amount of polyphenols ⁵⁸⁻⁶⁰. *Cistus monspeliensis* extract also has significant antioxidant activity ($IC_{50} = 0.077 \pm 0.009$ mg / mL) for the DPPH reduction test. This exciting result, which exceeds the antioxidant power of ascorbic acid ($IC_{50} = 0.082 \pm 0.012$ mg/mL), is probably due to its richness in various phenolic compounds identified by phytochemical tests. These molecules reduce the DPPH radical because of their ability to release a hydrogen atom ⁶¹⁻⁶³.

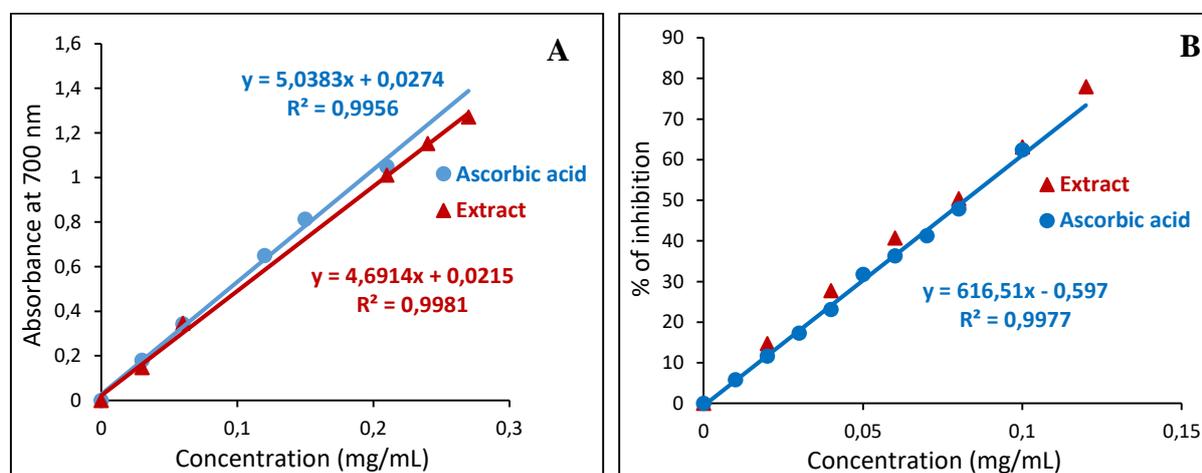


Figure 1. Variation of the absorbance obtained and the percentage of inhibition obtained as a function of the concentrations of *Cistus monspeliensis* extract compared with those of ascorbic acid. (A): FRAP test (B): DPPH test

Table 4. Results of the antioxidant capacity of the extract of *Cistus monspeliensis*, compared to that of ascorbic acid, expressed by the $IC_{0.5}$ and IC_{50} values obtained respectively in the FRAP and DPPH tests.

Antioxidant	FRAP $IC_{0.5}$ (mg/mL)	DPPH IC_{50} (mg/mL)
Ascorbic acid	0.093 ± 0.003	0.082 ± 0.012
extract	0.102 ± 0.006	0.077 ± 0.009

3.3. Potentiodynamic polarization measurements

Potentiodynamic anodic and cathodic polarization curves for ordinary steel in 1 M HCl solution in the absence and presence of different concentrations of *Cistus monspeliensis* extract at 298 K are shown in Figure 2. The kinetics parameters of the corrosion including corrosion potential E_{corr} , corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (β_c and β_a) and inhibition efficiency (η_{pp}) are represented in Table 5. It appears from these results that the addition of the extract decreases corrosion current density, indicating that the extracts retarded corrosion rate of ordinary steel samples in HCl solutions. Also, it can be seen that the inhibition

efficiency η_{pp} (%) of the extract increases with the inhibitor concentrations, to an optimum concentration (0.25 g/L), above that concentration, the value of this parameter decreased. Compared with the blank solution, when the change of the corrosion potential is above 85 mV, the inhibitor can be classified as cathodic or anodic, depending on the direction of displacement⁶⁴. Therefore, the corrosion potential (E_{corr}) of the ordinary steel has been cathodically displaced from 35 to 135 mV relatively to blank, indicating that the *Cistus monspeliensis* extract exhibits cathodic inhibition effects.

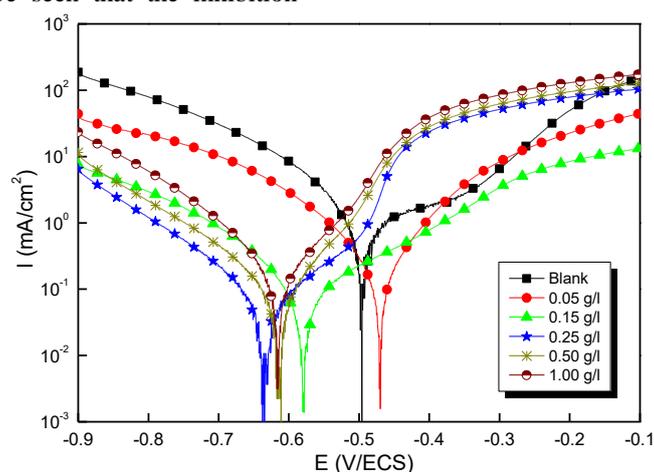


Figure 2. Polarization curves for ordinary steel in 1 M HCl at 298 K containing different concentrations of *Cistus monspeliensis* extract

Table 5. Electrochemical parameters of ordinary steel in 1 M HCl at 298 K containing different concentrations of *Cistus monspeliensis* extract.

Medium	Conc. g/L	$-E_{corr}$ mV/SCE	i_{corr} $\mu\text{A cm}^{-2}$	$-\beta_c$ mV dec ⁻¹	β_a mV dec ⁻¹	η_{pp} %
HCl 1.0 M	-	498	983	140	150	-
Extract	0.05	615	169	137	145	82.8
	0.15	614	128	132	140	86.9
	0.25	633	78	125	132	92.0
	0.50	576	112	118	135	88.6
	1.00	533	208	131	132	78.8

3.4. Electrochemical Impedance Spectroscopy

Electrochemical impedance diagrams relating to the ordinary steel / 1 M HCl interface in the absence and presence of *Cistus monspeliensis* extract at different concentrations are represented in Figure 3. The Nyquist plots show that the diameter increased for all concentrations. The analysis of the shape of these spectra exhibits that the curves are represented by a single capacitive semi-circle, showing that the corrosion was mainly controlled by charge transfer process⁶⁵.

The simple equivalent circuit, shown in Figure 4, is used to investigate technical details of impedance spectra. It allows calculating various parameters, such

as solution resistance R_s , charge transfer resistance R_{ct} , double layer capacitance C_{dl} and magnitude of constant phase element (CPE). CPE is used to give a more accurate fit. Its impedance function (Z_{CPE}) could be explained as follows⁶⁶:

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n}$$

Where Y_0 is the CPE constant, n is a CPE exponent which signifies interface surface properties of the working electrode, $j^2 = -1$ is the imaginary number, ω is the angular frequency in rad.s^{-1} ($\omega = 2\pi f$), and f is the frequency in Hz⁶⁷.

The double-layer capacitance (C_{dl}) is calculated from the equation:

$$C_{dl} = Q(\omega_{max})^{n-1}$$

Where $\omega_{max} = 2\pi f_{max}$ is the angular frequency at the maximum value of the imaginary part of the impedance spectrum, Q is the constant phase element (CPE).

The parameters associated with the impedance spectrums are reassembled in Table 6. As it can be seen from Table 5, the inhibitory efficiency increases to reach a maximum value 91.6%, polarization resistance R_{ct} increases from 23.36 to 279.60 $\Omega \text{ cm}^2$, Q and double-layer capacitance (C_{dl}) decreases from 190 to 65 $\mu\text{F} \cdot \text{cm}^{-2}$ with the increase of *Cistus monspeliensis* extract concentration until 0.25 g/L. The increase in R_{ct} values implied that an inhibitor-adsorption film was formed on the steel substrate, thus

retarding the charge transfer⁶⁸. The thickness of the electrical double layer is related to C_{dl} by the following equation⁶⁹:

$$\delta = \varepsilon_0 \varepsilon_r A / C_{dl}$$

Where ε_0 is the dielectric constant, ε_r is the relative dielectric constant, and A is the effective surface area. Therefore, a decrease in the capacity (C_{dl}) may be attributed to a decrease in the local dielectric constant of film, or an increase in the thickness of the electrical double layer, or both simultaneously occurred⁷⁰.

Hence, the results gave good agreement between the inhibition efficiency of corrosion as obtained from the impedance study and polarization measurement.

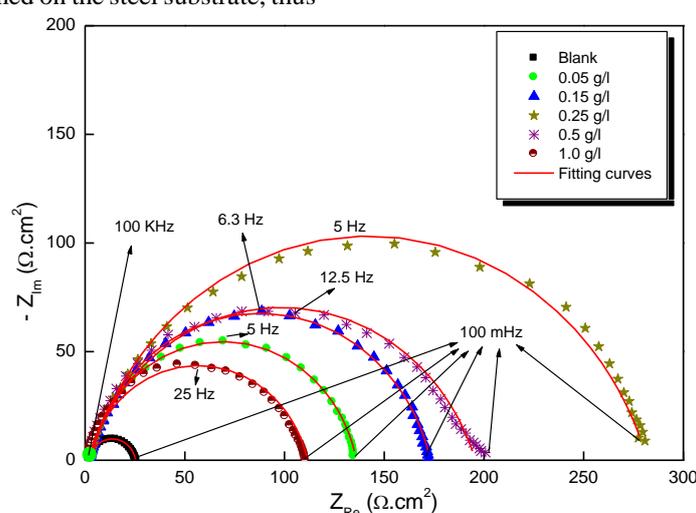


Figure 3. Nyquist diagrams for ordinary steel in 1 M HCl at 298 K in the absence and presence of different concentrations of *Cistus monspeliensis* extract

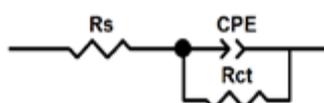


Figure 4. Equivalent electrochemical circuit for fitting the EIS experimental data

Table 6. Electrochemical impedance parameters in the absence and in the presence of the inhibitor at different concentrations.

Medium	Conc. (g/L)	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	n_{dl}	Q ($\mu\text{F} \cdot \text{S}^{n-1}$)	η_{imp} %
HCl 1.0M	--	1.9±0.3	23.36±0.5	190	0.897±0.02	470±1.9	-
Extract	0.05	2.2±0.1	133.8±0.4	105	0.871±0.01	363±1.3	82.5
	0.15	2.3±0.2	170.7±0.4	78	0.853±0.02	247±0.7	86.3
	0.25	2.3±0.2	279.6±0.4	65	0.809±0.01	127±0.3	91.6
	0.50	1.1±0.1	194.7±0.5	72	0.796±0.01	171±0.4	88.0
	1.00	1.5±0.2	109.6±0.5	59	0.854±0.02	123±0.7	78.6

3.5. Effect of temperature

3.5.1. Potentiodynamic polarization

Temperature is one of the parameters that can modify the behavior of a material in a corrosive environment. For that, we examined the effect of the temperature variation (298 K, 308 K, 318 K and 328 K), on the one

hand on the interactions of the metal with the corrosive solution in the absence and presence of the inhibitor, and its influence on the inhibitory efficacies on the other hand. This variation was studied by potentiodynamic polarization (Figure 5) in the presence of 0.25 g/L of *Cistus monspeliensis* extract.

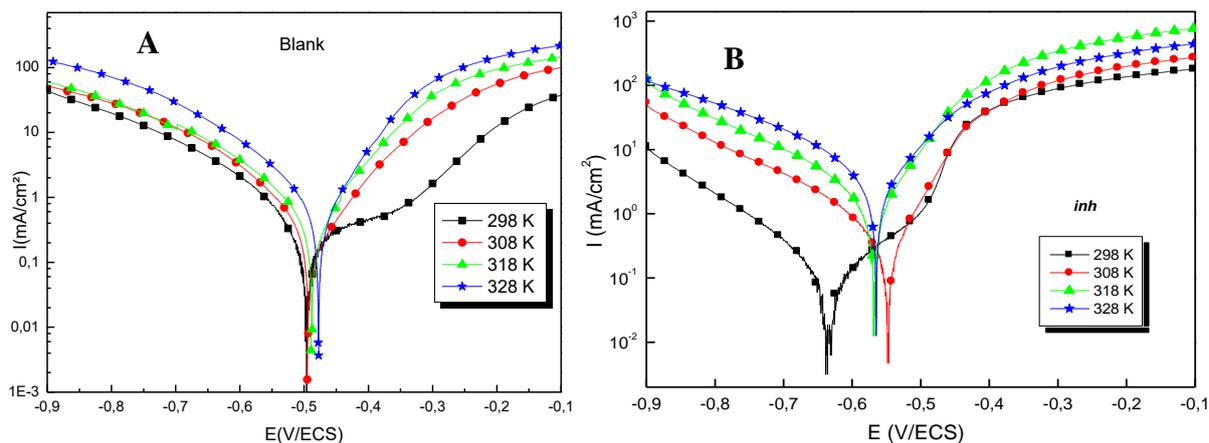


Figure 5. Polarization curves of ordinary steel in 1 M HCl in absence (A) and in the presence of inhibitor (B) at different temperatures

The values of the corrosion potential (E_{corr}), the corrosion current density (i_{corr}), the slopes of the anode β_a and cathode β_c and the inhibition efficiency (η_{pp}) are presented in Table 7. It appears that the corrosion current density increases while the inhibition efficiency decreases with the increase of the extracted temperature from 92.0% to 84.8% in 1 M

HCl. Which probably indicates desorption of inhibitor molecules^{71,72}. It can be seen also that the extract investigated have inhibitory properties at all temperatures studied, and the values of inhibition efficiency remain slightly constant with the increase in temperature.

Table 7. Electrochemical parameters for ordinary steel in 1 M HCl and the inhibitor 0.25 g/L at different temperatures.

Medium	Temperature K	$-E_{\text{corr}}$ mV/ECS	i_{corr} $\mu\text{A cm}^{-2}$	$-\beta_c$ mV dec ⁻¹	β_a mV dec ⁻¹	η_{PP} %
Blank	298	498	983	140	150	-
	308	491	1200	184	112	-
	318	475	1450	171	124	-
	328	465	2200	161	118	-
Extract	298	633	78	125	132	92.0
	308	547	122	172	110	89.8
	318	565	183	137	120	87.4
	328	563	333	151	114	84.8

3.5.2. Thermodynamic study

The thermodynamic study quantifies the inhibition efficiency against corrosion, facilitates the calculation of thermodynamic parameters, in exploring the activation energy and interpret the type of adsorption adopted by the inhibitor. Exploring the activation energy, the dependence of the corrosion current obtained was studied as a function of temperature, using Tafel extrapolation method (Figure 6). The corrosion reaction can be considered as an Arrhenius type process. Figure 6 (A), presents the Arrhenius plots of the natural logarithm of the current density versus $1/T$, for 1 M solution of hydrochloric acid, without and with the addition of *Cistus monspeliensis* extract. Straight lines with coefficients of correlation (c.c.) in the range 0.97354–0.99387 are obtained for the supporting electrolyte and the tested compound. The values of the slopes of these straight lines permit

the calculation of the Arrhenius activation energy by the following formula⁵⁴:

$$\ln i_{\text{corr}} = \ln A - \frac{E_a}{RT}$$

Where E_a is the apparent activation corrosion energy, T is the absolute temperature, A is the pre-exponential constant of Arrhenius and R is the universal gas constant. Table 7 shows the calculated values of apparent activation corrosion energy in the absence and presence of *Cistus monspeliensis* extract. It appears that E_a in the presence of inhibitor is higher than that corresponding to 1 M HCl solution. The increase in apparent activation energy can be interpreted as physical adsorption, which means that the inhibitor is adsorbed on the substrate by interaction electrostatic (weak bonds)^{54,73}. A previous study explained that the increase in activation energy

can be ascribed to a significant decrease in the adsorption of the inhibitor on the ordinary steel surface with an increase in temperature, with consequentially increased in corrosion of ordinary steel about the fact that the metal is exposed to the acid medium ^{71,74}.

An alternative formula of the Arrhenius equation makes it possible to determine the enthalpy and the entropy of activation according to the following equation:

$$\ln\left(\frac{i_{corr}}{T}\right) = \left[\ln\left(\frac{R}{hN_a}\right) + \left(\frac{\Delta S_a}{R}\right)\right] - \frac{\Delta H_a}{RT}$$

Where h is Planck's constant, N is Avogadro's number, ΔS_a is the entropy of activation, and ΔH_a is the enthalpy of activation.

Figure 6 (B) shows a plot of $\ln(i_{corr}/T)$ versus $1/T$. From the slope and the intercept of the straight lines,

the values of ΔH_a and ΔS_a are concluded respectively and listed in Table 8. Examination of these data revealed that the thermodynamic parameters (ΔH_a and ΔS_a) for dissolution reaction of ordinary steel in 1 M HCl in the presence of extract are higher than that obtained in the absence of inhibitor. The positive sign of enthalpies reflects the endothermic reaction of the steel dissolution process ⁷⁵. It is pointed out in the literature that a positive sign of the enthalpies reflects the endothermic nature of the steel dissolution process. The presence of inhibitors tested reveals that the corrosion process becomes more and more endothermic when compared to blank ⁷⁶.

The negative sign for the entropy of activation in both inhibited and uninhibited solutions indicates that the activation complex in rate determination step shows the association instead of the dissociation step, indicating that a decreased disorder occurs from reactant to the activated complex ⁷⁷.

Table 8. Thermodynamic parameters for the adsorption of *Cistus monspeliensis* extract in 1 M HCl on the ordinary steel at different temperatures.

Corrosive medium		Ea (KJ/mol)	ΔH_a (KJ/mol)	ΔS_a (J/mol.K)
HCl 1.0 M	Blank	21.0	18.5	-126.0
	Extract	38.5	35.9	-88.2

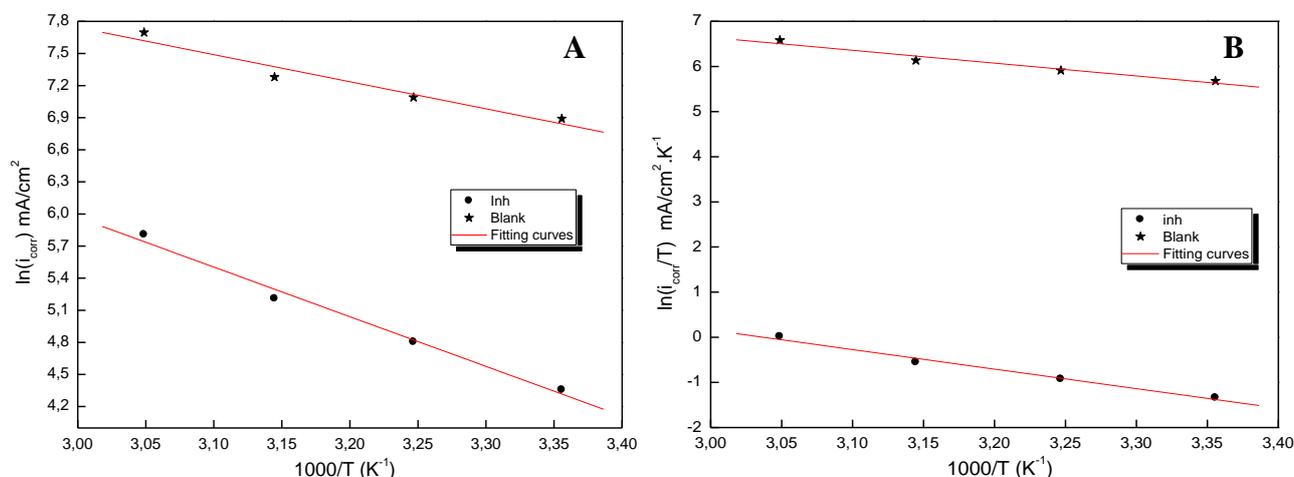


Figure 6. Arrhenius straights of ordinary steel in HCl medium 1 M without and with the addition of inhibitor

4. Conclusion

Based on this study, the following conclusions were derived:

- Phytochemical tests revealed the presence of several families of chemical compounds such as polyphenols (flavonoids, condensed tannins and hydrolysable tannins), saponins, glycosides, and reducing sugars.
- The antioxidant power of *Cistus monspeliensis* extract showed that this extract has an antioxidant capacity similar to that of ascorbic acid (the reference antioxidant). This activity seems to be related to the presence of phenolic compounds.

- The *Cistus monspeliensis* extract is efficient corrosion inhibitor for carbon steel in 1M HCl medium.

- Tafel plots showed that the extract is an excellent cathodic inhibitor.

- The effectiveness of the inhibition increases with increasing concentration of the extract to reach a maximum value of 92% at 0.25 g/L of *Cistus monspeliensis* extract.

- The extract remains active at the temperatures studied. The thermodynamic parameters obtained reveal physical adsorption between the extract and the surface of the metal.

- A correlation was observed between the measurements obtained from the potentiodynamic polarization curves and the electrochemical impedance spectroscopy techniques.
- The *Cistus monspeliensis* extract can find applications as well as in the medicinal and pharmaceutical fields than industrial.

References

- 1- M. Goyal, S. Kumar, I. Bahadur, C. Verma, E. E. Ebenso, Organic corrosion inhibitors for industrial cleaning of ferrous and non-ferrous metals in acidic solutions: A review, *J Mol Liq*, **2018**, 256, 565–573.
- 2- R. I. M. Asri, W. S. W. Harun, M. Samykano, N. A. C. Lah, S. A. C. Ghani, F. Tarlochan, M. R. Raza, Corrosion and surface modification on biocompatible metals: A review, *Mater Sci Eng C*, **2017**, 77, 1261–1274.
- 3- S. Mo, H.-Q. Luo, N.-B. Li, Plant extracts as “green” corrosion inhibitors for steel in sulphuric acid, *Chem Pap*, **2016**, 70, 1–13.
- 4- A. Sedik, D. Lerari, A. Salci, S. Athmani, K. Bachari, İ. H. Gecibesler, R. Solmaz, Dardagan Fruit extract as eco-friendly corrosion inhibitor for mild steel in 1 M HCl: Electrochemical and surface morphological studies, *J Taiwan Inst Chem Eng*, **2020**, 107, 189–200.
- 5- Y. Fang, B. Suganthan, R. P. Ramasamy, Electrochemical characterization of aromatic corrosion inhibitors from plant extracts, *J Electroanal Chem*, **2019**, 840, 74–83.
- 6- G. Bahlakeh, B. Ramezanzadeh, A. Dehghani, M. Ramezanzadeh, Novel cost-effective and high-performance green inhibitor based on aqueous Peganum harmala seed extract for mild steel corrosion in HCl solution: Detailed experimental and electronic/atomic level computational explorations, *J Mol Liq*, **2019**, 283, 174–195.
- 7- J. Halambek, I. Cindrić, A. Ninčević Grassino, Evaluation of pectin isolated from tomato peel waste as natural tin corrosion inhibitor in sodium chloride/acetic acid solution, *Carbohydr Polym*, **2020**, 234, 1–33.
- 8- A. El Moussaoui, F. Z. Jawhari, A. M. Almehdi, H. Elmsellem, K. Fikri Benbrahim, D. Bousta, A. Bari, Antibacterial, antifungal and antioxidant activity of total polyphenols of *Withania frutescens*.L, *Bioorganic Chem*, **2019**, 93, 1–18.
- 9- S. Ait Lahcen, L. El Hattabi, R. Benkaddour, N. Chahboun, M. Ghanmi, B. Satrani, M. Tabyaoui, A. Zarrouk, Chemical composition, antioxidant, antimicrobial and antifungal activity of Moroccan *Cistus Creticus* leaves, *Chem Data Collect*, **2020**, 26, 1–20.
- 10- M. Faustin, A. Maciuk, P. Salvin, C. Roos, M. Lebrini, Corrosion inhibition of C38 steel by alkaloids extract of *Geissospermum* leave in 1M hydrochloric acid: Electrochemical and phytochemical studies, *Corros Sci*, **2015**, 92, 287–300.
- 11- N. M’hiri, D. Veys-Renaux, E. Rocca, I. Ioannou, N. M. Boudhrioua, M. Ghoul, Corrosion inhibition of carbon steel in acidic medium by orange peel extract and its main antioxidant compounds, *Corros Sci*, **2016**, 102, 55–62.
- 12- A. Ehsani, M. G. Mahjani, M. Hosseini, R. Safari, R. Moshrefi, H. Mohammad Shiri, Evaluation of *Thymus vulgaris* plant extract as an eco-friendly corrosion inhibitor for stainless steel 304 in acidic solution by means of electrochemical impedance spectroscopy, electrochemical noise analysis and density functional theory, *J Colloid Interface Sci*, **2017**, 490, 444–451.
- 13- A. A. Khadom, A. N. Abd, N. A. Ahmed, Xanthium strumarium leaves extracts as a friendly corrosion inhibitor of low carbon steel in hydrochloric acid: Kinetics and mathematical studies, *South Afr J Chem Eng*, **2018**, 25, 13–21.
- 14- B. Ngouné, M. Pengou, A. M. Nouteza, C. P. Nanseu-Njiki, E. Ngameni, Performances of Alkaloid Extract from *Rauvolfia macrophylla* Stapf toward Corrosion Inhibition of C38 Steel in Acidic Media, *ACS Omega*, **2019**, 4, 9081–9091.
- 15- H. Elmsellem, Y. E. Ouadi, M. Mokhtari, H. Bendaif, H. Steli, Abdelouahed, Aouniti, A. M. Almehdi, I. Abdel-Rahman, H. S. Kusuma, B. Hammouti, A Natural Antioxidant and an Environmentally Friendly Inhibitor of Mild Steel Corrosion: A Commercial Oil of Basil (*OCIMUM BASILICUM* L.), *J Chem Techn Metall*, **2019**, 4, 742–749.
- 16- M. Ben Harb, S. Abubshait, N. Etteyeb, M. Kamoun, A. Dhouib, Olive leaf extract as a green corrosion inhibitor of reinforced concrete contaminated with seawater, *Arab J Chem*, **2020**, xxx, 1–11.
- 17- A. Zaher, A. Chaouiki, R. Salghi, A. Boukhraz, B. Bourkhiss, M. Ouhssine, Inhibition of Mild Steel Corrosion in 1M Hydrochloric Medium by the Methanolic Extract of *Ammi visnaga* L. Lam Seeds, *Int J Corros*, **2020**, 2020, 1–10.
- 18- A. Dehghani, G. Bahlakeh, B. Ramezanzadeh, A detailed electrochemical/theoretical exploration of the aqueous Chinese gooseberry fruit shell extract as green and cheap corrosion inhibitor for mild steel in acidic solution, *J Mol Liq*, **2019**, 282, 366–384.
- 19- Z. Sanaei, M. Ramezanzadeh, G. Bahlakeh, B. Ramezanzadeh, Use of *Rosa canina* fruit extract as a green corrosion inhibitor for mild steel in 1M HCl solution: A complimentary experimental, molecular dynamics and quantum mechanics investigation, *J Ind Eng Chem*, **2019**, 69, 18–31.
- 20- F. Bouhlal, N. Labjar, F. Abdoun, A. Mazkour, M. Serghini-Idrissi, M. El Mahi, E. M. Lotfi, S. El Hajjaji, Electrochemical and Thermodynamic Investigation on Corrosion Inhibition of C38 Steel in 1M Hydrochloric Acid

- Using the Hydro-Alcoholic Extract of Used Coffee Grounds, *Int J Corros*, **2020**, 2020, 1–14.
- 21-G. Mouhsine, K. Tarfaoui, M. Ouakki, M. Nehiri, M. E. Touhami, N. Barhada, M. Ouhsine, Valorization of the essential oil of Zingiber officinale by its Use as inhibitor against the corrosion of the carbon steel in acid medium hydrochloric acid 1M, *Mediterr J Chem*, **2019**, 8, 17–24.
- 22-R. Haldhar, D. Prasad, N. Bhardwaj, Surface Adsorption and Corrosion Resistance Performance of Acacia concinna Pod Extract: An Efficient Inhibitor for Mild Steel in Acidic Environment, *Arab J Sci Eng*, **2020**, 45, 131–141.
- 23-Z. Bensouda, E. H. El Assiri, M. Sfaira, M. Ebn Touhami, A. Farah, B. Hammouti, Extraction, Characterization and Anticorrosion Potential of an Essential Oil from Orange Zest as Eco-friendly Inhibitor for Mild Steel in Acidic Solution, *J Bio- Tribo-Corros*, **2019**, 5, 1–20.
- 24-A. Foda, H. Mosallam, A. El-Khateeb, M. Fakhri, Cinnamomum zeylanicum Extract as Green Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid Solutions, *Prog Chem Biochem Res*, **2019**, 2, 120–133.
- 25-J. S. Ribeiro, M. J. M. C. Santos, L. K. R. Silva, L. C. L. Pereira, I. A. Santos, S. C. da Silva Lannes, M. V. da Silva, Natural antioxidants used in meat products: A brief review, *Meat Sci*, **2019**, 148, 181–188.
- 26-S. Salekzamani, M. Ebrahimi-Mameghani, K. Rezazadeh, The antioxidant activity of artichoke (*Cynara scolymus*): A systematic review and meta-analysis of animal studies: Antioxidant activity of artichoke (*Cynara Scolymus*), *Phytother Res*, **2019**, 33, 55–71.
- 27-D. Stagos, Antioxidant Activity of Polyphenolic Plant Extracts, *Antioxidants*, **2019**, 9, 1–7.
- 28-M. H. Khawory, A. Amat Sain, M. A. A. Rosli, M. S. Ishak, M. I. Noordin, H. A. Wahab, Effects of gamma radiation treatment on three different medicinal plants: Microbial limit test, total phenolic content, in vitro cytotoxicity effect and antioxidant assay, *Appl Radiat Isot*, **2020**, 157, 1–42.
- 29-S. Sethi, A. Joshi, B. Arora, A. Bhowmik, R. R. Sharma, P. Kumar, Significance of FRAP, DPPH, and CUPRAC assays for antioxidant activity determination in apple fruit extracts, *Eur Food Res Technol*, **2020**, 246, 591–598.
- 30-A. Ácsová, S. Martiniaková, J. Hojerová, Selected in vitro methods to determine antioxidant activity of hydrophilic/lipophilic substances, *Acta Chim Slovaca*, **2019**, 12, 200–211.
- 31-M. Lewoyehu, M. Amare, Comparative evaluation of analytical methods for determining the antioxidant activities of honey: A review, *Cogent Food Agric*, **2019**, 5, 1–24.
- 32-S. M. S. S. A. Rifki, S. M. S.A.Rifki, S. O. S. Hassane, S. Haida, K. Bakkouche, A. Kribii, A. Kribii, Phytochemical Study and Evaluation of the Antioxidant Activity of Extracts of *Plectranthus Aromaticus* Originating in the Island of Great Comoros, *J Pharm Pharm*, **2019**, 6, 83–88.
- 33-A. Agnieszka Stępień, D. David Aebisher, D. Dorota Bartusik-Aebisher, Biological properties of *Cistus* species, *Eur J Clin Exp Med*, **2018**, 16, 127–132.
- 34-S. A. Mignacca, M. Mucciarelli, E. Colombino, E. Biasibetti, S. Muscia, B. Amato, V. D. M. L. Presti, I. Vazzana, A. Galbo, M. T. Capucchio, *Cistus salviifolius* Toxicity in Cattle, *Vet Pathol*, **2020**, 57, 115–121.
- 35-M. Latos-Brozio, A. Masek, Effect of Impregnation of Biodegradable Polyesters with Polyphenols from *Cistus linnaeus* and *Juglans regia* Linnaeus Walnut Green Husk, *Polymers*, **2019**, 11, 1–17.
- 36-D. D. Kiliç, B. Siriken, Ö. Ertürk, G. Tanrikulu, M. Gül, C. Baskan, Antibacterial, Antioxidant and DNA Interaction Properties of *Cistus creticus* L. Extracts, *J Int Environ Appl Sci*, **2019**, 14, 110–115.
- 37-K. Sayah, I. Marmouzi, H. Naceiri Mrabti, Y. Cherrah, M. E. A. Faouzi, Antioxidant Activity and Inhibitory Potential of *Cistus salviifolius* (L.) and *Cistus monspeliensis* (L.) Aerial Parts Extracts against Key Enzymes Linked to Hyperglycemia, *BioMed Res Int*, **2017**, 2017, 1–7.
- 38-K. Sayah, L. Chemlal, I. Marmouzi, M. El Jemli, Y. Cherrah, M. E. A. Faouzi, In vivo anti-inflammatory and analgesic activities of *Cistus salviifolius* (L.) and *Cistus monspeliensis* (L.) aqueous extracts, *South Afr J Bot*, **2017**, 113, 160–163.
- 39-J. Xiang, F. B. Apea-Bah, V. U. Ndolo, M. C. Katundu, T. Beta, Profile of phenolic compounds and antioxidant activity of finger millet varieties, *Food Chem*, **2019**, 275, 361–368.
- 40-Y. Jiao, S. Y. Quek, M. Gu, Y. Guo, Y. Liu, Polyphenols from thinned young kiwifruit as a natural antioxidant: Protective effects on beef oxidation, physicochemical and sensory properties during storage, *Food Control*, **2020**, 108, 1–9.
- 41-A. Piga, P. Duce, C. Cesaraccio, Phenological growth stages of Montpellier Rock-Rose Mediterranean shrub (*Cistus monspeliensis*): codification and description according to the BBCH scale, *Ann Appl Biol*, **2018**, 172, 384–391.
- 42-M. Berekci, H. Hassaine, C. Bekhechi, D. Abdelouahid, Evaluation of Antibacterial Activity of some Medicinal Plants Extracts Commonly Used in Algerian Traditional Medicine against some Pathogenic Bacteria, *Pharmacogn J*, **2018**, 10, 507–512.
- 43-H. Karim, H. Boubaker, L. Askarne, I. Talibi, F. Msanda, E. H. Boudyach, B. Saadi, A. Ait Ben Aoumar, Antifungal properties of organic

- extracts of eight *Cistus* L. species against postharvest citrus sour rot, *Lett Appl Microbiol*, **2016**, 62, 16–22.
- 44-I. Cocan, E. Alexa, C. Danciu, I. Radulov, A. Galuscan, D. Obistioiu, A. A. Morvay, R. M. Sumalan, M.-A. Poiana, G. Pop, C. A. Dehelean, Phytochemical screening and biological activity of Lamiaceae family plant extracts, *Exp Ther Med*, **2018**, 15, 1863–1870.
- 45-K. Ngibad, Phytochemical Screening of Sunflower Leaf (*Helianthus annuus*) and Anting-Anting (*Acalypha indica* Linn) Plant Ethanol Extract, *Borneo J Pharm*, **2019**, 2, 24–30.
- 46-A. A. Tuama, A. A. Mohammed, Phytochemical screening and in vitro antibacterial and anticancer activities of the aqueous extract of *Cucumis sativus*, *Saudi J Biol Sci*, **2019**, 26, 600–604.
- 47-R. Gul, S. U. Jan, S. Faridullah, S. Sherani, N. Jahan, Preliminary Phytochemical Screening, Quantitative Analysis of Alkaloids, and Antioxidant Activity of Crude Plant Extracts from *Ephedra intermedia* Indigenous to Balochistan, *Sci World J*, **2017**, 2017, 1–7.
- 48-S. Haida, F. Essadik, A. Kribii, A. Habsaoui, O. Khadija, A. Benmoumen, A. Kribii, Study of Chemical Composition of Rosemary Essential Oil From Western Morocco and Evaluation of Antioxidant and Antibacterial Activity of Its Extracts, *World J Pharm Res*, **2015**, 4, 307–323.
- 49-C. Yin, L. Xie, Y. Guo, Phytochemical analysis and antibacterial activity of *Gentiana macrophylla* extract against bacteria isolated from burn wound infections, *Microb Pathog*, **2018**, 114, 25–28.
- 50-F. Z. Essadik, S. Haida, A. Kribii, A. R. Kribii, K. Ounine, A. Habsaoui, Antioxidant activity of *Citrus aurantium* L. var. *amara* Peel from western of Morocco, identification of volatile compounds of its essential oil by GC-MS and a preliminary study of their antibacterial activity, *Int J Innov Sci Res*, **2015**, 16, 425–432.
- 51-Jo. Olugbami, M. Gbadegesin, O. A. Odunola, In vitro free radical scavenging and antioxidant properties of ethanol extract of *Terminalia glaucescens*, *Pharmacogn Res*, **2015**, 7, 49–56.
- 52-S. Gonçalves, T. Grevenstuck, N. Martins, A. Romano, Antioxidant activity and verbascoside content in extracts from two uninvestigated endemic *Plantago* spp, *Ind Crops Prod*, **2015**, 65, 198–202.
- 53-L. Estevinho, A. P. Pereira, L. Moreira, L. G. Dias, E. Pereira, Antioxidant and antimicrobial effects of phenolic compounds extracts of Northeast Portugal honey, *Food Chem Toxicol*, **2008**, 46, 3774–3779.
- 54-M. Ouakki, M. Galai, M. Cherkaoui, E.-H. Rifi, Z. Hatim, Inorganic compound (Apatite doped by Mg and Na) as a corrosion inhibitor for mild steel in phosphoric acidic medium, *Anal Bioanal Electrochem*, **2018**, 10, 943–960.
- 55-A. Ostovari, S. M. Hoseinie, M. Peikari, S. R. Shadzadeh, S. J. Hashemi, Corrosion inhibition of mild steel in 1M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawson, Gallic acid, α -D-Glucose and Tannic acid), *Corros Sci*, **2009**, 51, 1935–1949.
- 56-H. Karim, H. Boubaker, L. Askarne, K. Cherifi, H. Lakhtar, F. Msanda, E. H. Boudyach, A. Ait Ben Aoumar, Use of *Cistus* aqueous extracts as botanical fungicides in the control of Citrus sour rot, *Microb Pathog*, **2017**, 104, 263–267.
- 57-A. Bouyahya, Determination of Phenol Content and Antibacterial Activity of Five Medicinal Plants Ethanolic Extracts from North-West of Morocco, *J Plant Pathol Microbiol*, **2016**, 07, 1–4.
- 58- I. Hmid, D. Elothmani, H. Hanine, A. Oukabli, E. Mehinagic, Comparative study of phenolic compounds and their antioxidant attributes of eighteen pomegranates (*Punica granatum* L.) cultivars grown in Morocco, *Arabian Journal of Chemistry*, **2017**, 10, 1–10.
- 59-V. Viswanath, A. Urooj, N. G. Malleshi, Evaluation of antioxidant and antimicrobial properties of finger millet polyphenols (*Eleusine coracana*), *Food Chem*, **2009**, 114, 340–346.
- 60-A. Altemimi, R. Choudhary, D. G. Watson, D. A. Lightfoot, Effects of ultrasonic treatments on the polyphenol and antioxidant content of spinach extracts, *Ultrason Sonochem*, **2015**, 24, 247–255.
- 61-S. B. Nimse, D. Pal, Free radicals, natural antioxidants, and their reaction mechanisms, *RSC Adv*, **2015**, 5, 27986–28006.
- 62-M. C. Foti, Use and Abuse of the DPPH[•] Radical, *J Agric Food Chem*, **2015**, 63, 8765–8776.
- 63-M. Jabbari, A. Jabbari, Antioxidant potential and DPPH radical scavenging kinetics of water-insoluble flavonoid naringenin in an aqueous solution of micelles, *Colloids Surf Physicochem Eng Asp*, **2016**, 489, 392–399.
- 64-A. Dehghani, G. Bahlakeh, B. Ramezanzadeh, M. Ramezanzadeh, Potential of Borage flower aqueous extract as an environmentally sustainable corrosion inhibitor for acid corrosion of mild steel: Electrochemical and theoretical studies, *J Mol Liq*, **2019**, 277, 895–911.
- 65-P. Singh, S. S. Chauhan, G. Singh, M. A. Quraishi, Corrosion Inhibition by Green Synthesized Inhibitor: 4,4'-(1,4Phenylene)bis(6-amino-3-methyl-2,4dihydropyrano[2,3-c]pyrazole-5 carbonitrile) for Mild Steel in 0.5 M H₂SO₄ Solution, *J Bio- Tribo-Corros*, **2019**, 5, 1–9.
- 66-S. Cao, D. Liu, H. Ding, J. Wang, H. Lu, J. Gui, Corrosion inhibition effects of a novel ionic liquid with and without potassium iodide for carbon steel in 0.5 M HCl solution: An experimental study and the theoretical calculation, *J Mol Liq*, **2019**, 275, 729–740.
- 67-M. A. Bedair, S. A. Soliman, M. A. Hegazy, I. B. Obot, A. S. Ahmed, Empirical and theoretical investigations on the corrosion inhibition

- characteristics of mild steel by three new Schiff base derivatives, *J Adhes Sci Technol*, **2019**, 33, 1139–1168.
- 68- Y. Qiang, S. Zhang, B. Tan, S. Chen, Evaluation of Ginkgo leaf extract as an eco-friendly corrosion inhibitor of X70 steel in HCl solution, *Corros Sci*, **2018**, 133, 6–16.
- 69- H. M. Elabbasy, A. S. Fouda, Olive leaf as a green corrosion inhibitor for C-steel in Sulfamic acid solution, *Green Chem Lett Rev*, **2019**, 12, 332–342.
- 70- M. Ouakki, M. Rbaa, M. Galai, B. Lakhrissi, E. H. Rifi, M. Cherkaoui, Experimental and Quantum Chemical Investigation of Imidazole Derivatives as Corrosion Inhibitors on Mild Steel in 1.0 M Hydrochloric Acid, *J Bio- Tribo- Corros*, **2018**, 4, 1–14.
- 71- T. Rabizadeh, S. K. Asl, Casein as a natural protein to inhibit the corrosion of mild steel in HCl solution, *J Mol Liq*, **2019**, 276, 694–704.
- 72- H. Derfouf, Y. Harek, L. Larabi, W. J. Basirun, M. Ladan, Corrosion inhibition activity of carbon steel in 1.0 M hydrochloric acid medium using *Hammada scoparia* extract: gravimetric and electrochemical study, *J Adhes Sci Technol*, **2019**, 33, 808–833.
- 73- E. B. Ituen, M. M. Solomon, S. A. Umoren, O. Akaranta, Corrosion inhibition by amitriptyline and amitriptyline based formulations for steels in simulated pickling and acidizing media, *J Pet Sci Eng*, **2019**, 174, 984–996.
- 74- A. K. Singh, M. A. Quraishi, Effect of Cefazolin on the corrosion of mild steel in HCl solution, *Corros Sci*, **2010**, 52, 152–160.
- 75- O. Fergachi, F. Benhiba, M. Rbaa, M. Ouakki, M. Galai, R. Touir, B. Lakhrissi, H. Oudda, M. E. Touhami, Corrosion Inhibition of Ordinary Steel in 5.0 M HCl Medium by Benzimidazole Derivatives: Electrochemical, UV–Visible Spectrometry, and DFT Calculations, *J Bio- Tribo- Corros*, **2019**, 5, 1–13.
- 76- M. Dahmani, A. Et-touhami, S. S. Al-deyab, B. Hammouti, A. Bouyanzer, Corrosion Inhibition of C38 Steel in 1 M HCl: A Comparative Study of Black Pepper Extract and Its Isolated Piperine, **2010**, 5.
- 77- G. Khan, W. J. Basirun, S. N. Kazi, P. Ahmed, L. Magaji, S. M. Ahmed, G. M. Khan, M. A. Rehman, A. B. B. M. Badry, Electrochemical investigation on the corrosion inhibition of mild steel by Quinazoline Schiff base compounds in hydrochloric acid solution, *J Colloid Interface Sci*, **2017**, 502, 134–145.