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Date Palm Waste Extract as Corrosion Inhibitor for 304 Stainless Steel in 1 M HCl Solution

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The inhibiting action of date palm waste extract, as a natural inhibitor on corrosion of 304 stainless steel in 1M HCl solution, was investigated via potentiodynamic polarization and electrochemical impedance spectroscopy EIS techniques. The results indicate that, the extract act as a mixed-type with an anodic predominance; 91.1 % inhibition efficiency, was achieved when 1, 5 $g.L^{-1}$ of extract is added. Impedance curves show that, the double layer capacity decreases as the concentration of the extract increases.

Keywords: Corrosion; 304 stainless steel; date palm extract; Polarization; EIS; 1M HCl solution.

1. INTRODUCTION

The phenomenon of corrosion affects most industrial sectors and causes important financial damage [1]. In most industrial processes, metals exposed to acids test as corrosive agents. These acids play an important role in the industry and their substitution is very complex, especially in crude oil refining, acid pickling, industrial cleaning, acid scaling, and in petrochemical processes [2, 3]. Hydrochloric acid is one of the most widely used agents in the industrial sector; it causes degradation of metals either by chemical or electrochemical reactions. In order to prevent or delay the corrosion of metallic materials, there are many several methods [4-6].

The use of natural inhibitors extracted directly from oils or plants is a promising alternative, which given at the same time an excellent inhibitory power at low concentration and an ecological character of the products, their low cost contribute to their use at different fields[7-10].

Several extract was tested to control the corrosion rate of metals in corrosive environment; they had demonstrated significant inhibitory efficiencies. Abboud and al. [11] were tested the effect of the extract of brown alga BB on the corrosion of carbon steel in a 1M HCl medium. This extract allows achieving an inhibitor efficiency of 76% at 50% (v / v), the extract react as mixed behaviour with predominant of anodic efficacy at higher concentrations. Under the same conditions and on the same type of metal, this research team carried out another work. The effect of pomegranate and apples peel extract on the corrosion in a 1M HCl medium, by the addition of 1 g / L of the extract they reported an inhibitor efficiency of 80%, the extract showed a mixed character and inhibition was carried out by adsorption according to the Langmuir model [12].

The corrosion of the steel IS 226 was studied by Nahle and al. [13], they were used the extracted from UAE Neem (Azadirachta Indica), the results obtained showed an efficiency of 87% for 2 g / l in HCl (1M) medium at an ambient temperature, this rate decreases to (80%) in higher temperatures 303K. The corrosion of 1018 steel was studied by Inzunza and al. [14], the ethanolic extract of the leaves of Pachycormus discolor was used as an inhibitor in HCl (1M) medium, the obtained results showed that at 25 ° C. The efficiency is 94.52%, and at 75 ° C the efficiency reaches 97.89% for a concentration of 2% v / v. Soltani and al. [15] tested the effect of S. officinalis extract on the corrosion of 304 stainless steel in 1M HCl, which showed that increasing the concentration of the inhibitor boost the inhibitor efficiency to reach 96.6% when 2 g/ L of the inhibitor was added, the adsorption process is spontaneous and follows the Langmuir adsorption isotherm.

The aim of this work is to study the effect of date palm waste extract on the corrosion of 304 stainless steel in 1M HCl. It constitutes for Moroccan Saharan regions an essential element of the oasis ecosystem and it plays an important role not only due to its economic importance, but also to its ecological adaptation allowing ensure a necessary protection for cultures in underlying against the hard climatic conditions (hot, dry winds,… ect), also contribute to the fight against the silting up. However, in the periodic maintenance the materials generals significant quantities of waste, which is considered a threat to the environment and a very useful loss of organic compounds.

Many studies have demonstrated that these wastes are rich in organic matter and considered as noble products, which became a new raw materials for many industries. Oushabi and al. [16] have studied date palm wood waste in the field of thermal insulation, they have reported that, this waste must be treated in order to eliminate the amount of hemicellulose and lignin in order to increase their mechanical and thermal characteristics, and increase the adhesion with other materials. The manuscript reports on the effects of date palm waste extract on the corrosion behaviour of 304 stainless steel in 1 M HCl solution. Corrosion inhibition effect was investigated by using electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PDP) techniques complemented by surface analysis using optical microscope. The subject matter of interest in the fields of materials especially corrosion, it's focused on the environmental use of green materials in corrosion corrosion control.

2. MATERIALS AND METHODS

2.1. Preparation of plant extract

The date palm extract was prepared from its waste and was recovered, cleaned and then reduced to fine particles by crushing and ground. The sample was washed with double-distilled water and then dried at ambient temperature. Briefly, a sample mass of 250 g was poured in a flask of 500 ml containing a solution of 1M hydrochloric acid, the mixture was brought to ambient temperature for

24 hours, and then boiling with reflux for 2 hours. The obtained extract was filtered and placed on the rotary evaporator to remove the solvent. The sample was dried and added to the corrosive solutions.

2.2. Electrodes and solutions

The working electrode used in the experiment was a 304 stainless steel (18% Cr, 8% Ni, 2% Mn, 0.08% C and remaining Fe). Before any measurements, the materials submitted a mechanical polishing via a various emery paper grades (220, 400, 600, 1000, 1200 and 2000) in a decreasing way. The electrodes were then degreased in acetone, rinsed with double-distilled water and finally dried at room temperature. The 1M corrosive solutions were prepared from double-distilled water and HCl of purity 37% and density 1.2 g / mL. The extract is added in g/l for all the prepared solutions.

2.3. Electrochemical measurements

The electrochemical measurements were carried out in a conventional three-electrode cell; using the OGS 080 Origalys type Galvanostat potentiostat. The devise was connected to a computer via the interface origaMaster 5, Vesrion 2.1.0.3 Copyright © 2014, the 0.1 M Hg / HgO electrode; the auxiliary electrode and the working electrodes were used as the reference electrode, platinium wire and were based on 304 stainless steel respectively. During the test, a 100 ml of sample is taken each time from cell. In order to reach the steady state and the open circuit potential, the electrodes are emerged for 60 minutes in the electrolytes.

For a high precision, the polarization measurements were carried out in the ranges of -600 to -200 mV with a sweep rate of 0.5mV/s. The spectroscopic impedance measurements (EIS) were performed at corrosion potentials (Ecor) and recorded in the range of 1 KHz to 10 MHz with amplitude of 10 mV. The inhibitors efficiencies are calculated using the equations 1 and 2:

$$\eta Taf(\%) = \frac{Icorr - Icorr(ex)}{Icorr} \times 100 \quad (1)$$

$$\eta EIS(\%) = \frac{Rct\ (ex) - Rct}{Rct(ex)} \times 100 \quad (2)$$

Where Icorr, Icorr (ex) (the current densities) and Rct, Rct (ex) (the charge transfer resistors) in the absence and in the presence of the inhibitor for each of two.

2.4. Surface analysis

After an immersion in the HCl medium in the presence and absence of the extract, the electrode surface was determined by using the optical metallographic microscopy. Hence, characterizing the state of degradation of samples after a various corrosion tests. The microscope is a Nikon Epiphot coupled with a digital camera.

The optical metallographic microscopy was used for determined the electrode surface after immersion in the HCl medium in the presence and absence of the extract, so as to characterize the state of degradation of the samples after the various tests of corrosion. The microscope used in this study is a Nikon Epiphot microscope coupled to a digital camera.

2.5. FTIR spectrophotometry

Sample and the films deposited on surface electrode characterized by FT-IR spectroscopy Mattson 7000 spectrophotometer. Ten scans were collected (wave ranging from 4000 to 500 cm-1) to obtain FTIR spectra.

3. RESULTS AND DISCUSSION

3.1. Electrochemical measurements

3.1.1. Open Circuit Potential (OCP)

To record the open-circuit electrode potential, all solutions were immersed 60 minutes at ambient temperature.

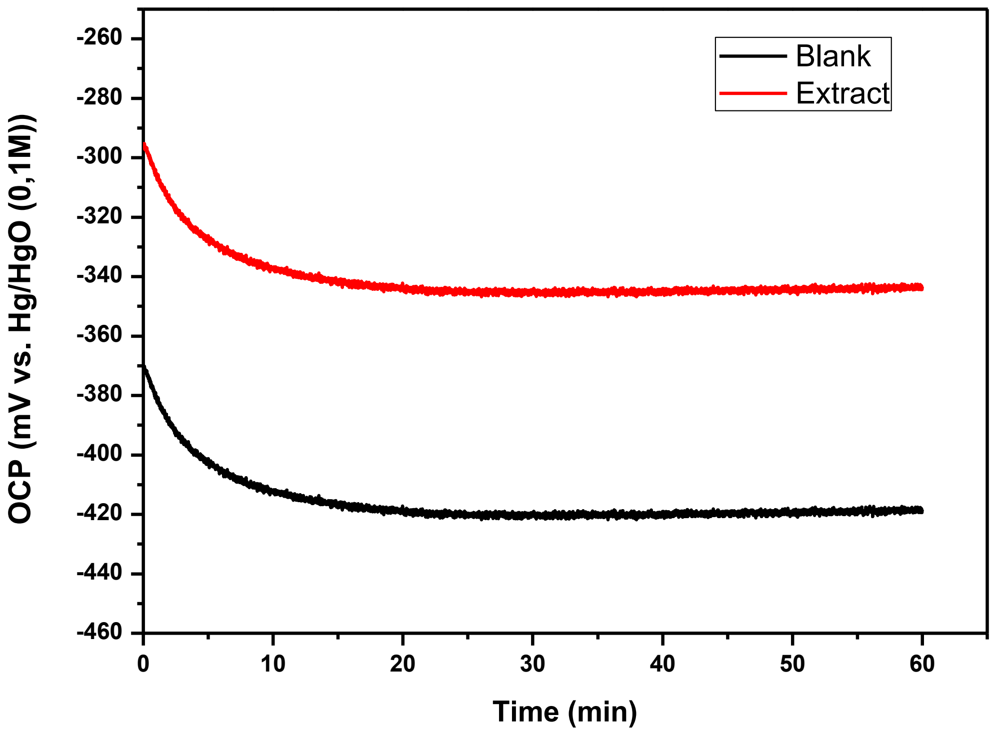

Figure 1. Open circuit potential evolution of stainless steel 304 in 1M HCl solution without and in the presence of 1.5g/L date palm waste extract.

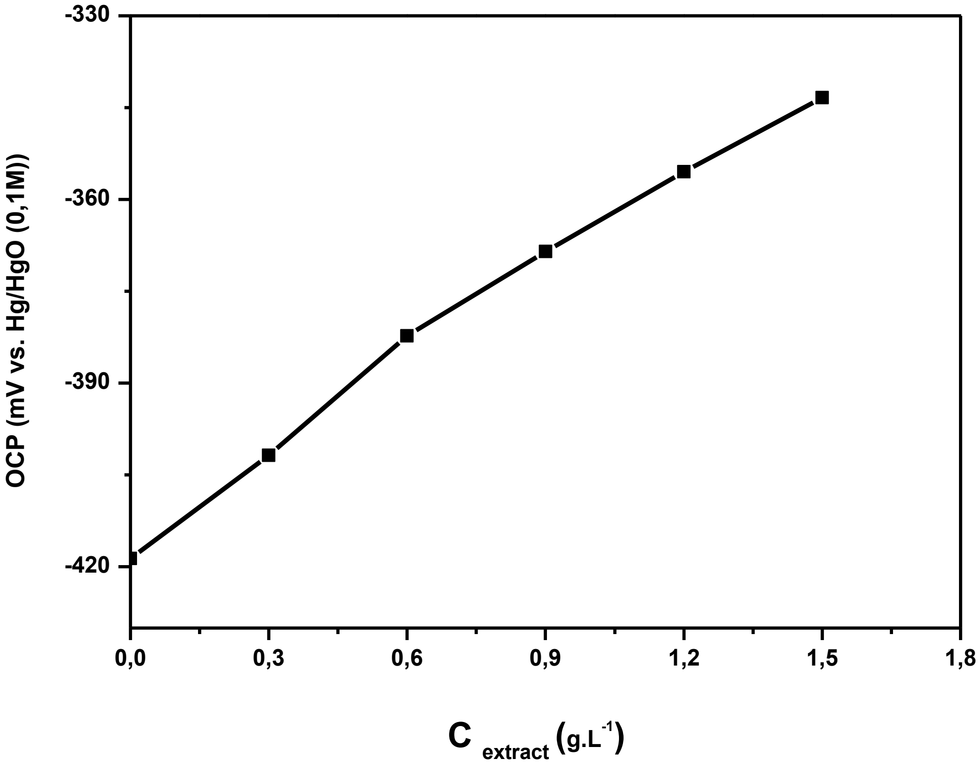

Figure 2. The variation in OCP values in 1M HCl solution containing different concentrations of date palm waste at 25°C for 1 h of immersion.

The potential of stainless steel stabilized after 10 min of immersion as illustrated in Figure1. The OCP drop out potential remains constant around -420 mV in absence of the extract. The low negative value is due to the corrosive product soluble at the surface of the electrode, which destabilizes the protective film [17]. However, the OCP drop potential reached -340 mV in the presence of extract. It characterized the genesis of the protective film which contributes to the stabilization of the passivation layer in the corrosive medium even after prolonged immersion [18].

Figure 2 show the effect of the extract concentration on the OCP, according to the graph it is noted that the addition of the extract leads to the displacement of the potential towards more positive values. This makes it possible to conclude that the increased concentration of the extract in the medium increases the protective capacity of the stainless steel 304 against corrosion [18].

3.1.2. Polarization measurements

In order to study the effect of the extract on the polarization behaviour of stainless steel, the polarization curves at different concentrations of extract in 1M HCl medium were recorded at room temperature, they are given in Figure 3. The analysis of the curves makes it possible to observe that the increase in the concentration of extract, leads to the reduction of the corrosion current densities (Icorr), in a significant manner. The test results indicated that the extract inhibitor preferentially inhibited and suppressed the anodic reaction more than the cathodic reaction. The extract inhibitory efficiency increases by increasing the extract concentration.

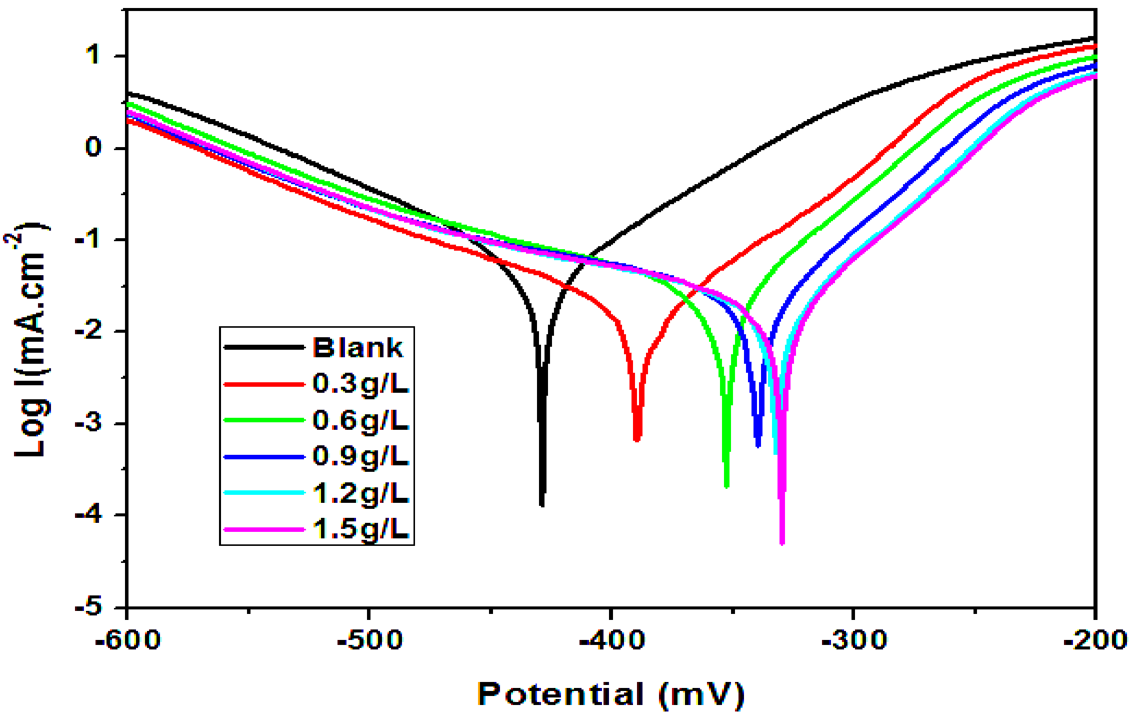

Figure 3. Polarization curves of stainless steel 304 obtained after 1 h in 1 M HCl solution in the absence (blank) and presence of different concentrations of date palm waste extract at 25°C.

The values of corrosion parameters, corrosion potential (Ecor), current density (icor), Tafel slopes (cathode and anodic beta) and inhibitory efficiency are given in Table 1.

Table 1. Polarization parameters for 304 stainless steel in 1M HCl solutions in the presence and absence of date palm waste extract

C extract (g L-1)	Ecorr (mV)	βc (mV dec-1)	Ba (mV dec-1)	Icorr (µA cm-2)	CR (µm year-1)	η Tafel (%)
Blank	-428.7	85.9	70.4	53.9	630.61	---------
0.3	-389.2	105.3	53.8	15.1	177.19	71.98
0.6	-353.1	105.7	40.3	11.4	133.46	78.85
0.9	-340.0	108.2	37.1	7.3	85.127	86.45
1.2	-332.4	103.0	35.6	5.2	60.675	90.35
1.5	-329.8	102.5	35.4	4.8	56.65	91.09

The action of the extract results, in a decrease in corrosion currents of 53.9 µA cm^{-2} for the medium without extract at 4.3 µA cm^{-2} when 1.5 g/L of the extract is added. This result shows that the addition of the extract reduces the anodic dissolution of the steel and delays the evolution of the H + ion discharge [19]. The decrease in the density of the corrosion current, is due to the blocking effect of the active sites on the metal surface by the adsorbed molecules of the extract [20]. The corrosion potential varies with the concentration of the extract, confirming the mixed character of this inhibitor, in the vicinity of the potential -280 mV a pseudo plateau is observed for all the recorded curves is perhaps due to a desorption of a certain amount of the adsorbed material. The average corrosion rates determined from the polarization curves, demonstrate that corrosion rate reached a maximum of 600 µm.year^{-1} in 1 M HCl solution and decreased to an average value of 56.65 µm.year^{-1} when 1.5 g/L of the inhibitor is added.

The inhibitory efficiency reaches 91.07% when 1.5g / l of the extract is added; this value is comparable with those mentioned in the literature. Table 2 shows some inhibitory efficacy found for inhibitors already used. The analysis of the results shows inhibitory efficiencies ranging from 49% for 2% (V / V) of Thymus vulgaris plant extract to 96.4% for 1 g / L of Silybum marianum leaf extract.

Table 2. Inhibitory efficiency of some work on 304 stainless steel in acid medium

Inhibitor source	Metal type	Middle	Inhibitor concentration	EI (%)	Ref
Thymus vulgaris plant extract	Stainless steel 304	1M HCl	2% (V/V)	49	[21]
4-phenylthiazole derivatives	Stainless steel 304	3M HCl	11.10^{-6}M	69.4	[22]
Substitute pyrazolones	Stainless steel 304	0.5M H2SO4	1.10^{-2}M	71.88	[23]
5-Sulphadiazineazo-3-phenyl-2-thioxo-4-thiazolidinone	Stainless steel 304	1M HCl	1.10^{-3}M	84.24	[24]
Schiff bases	Stainless steel 304	1M HCl	1.10^{-3}M	84.7	[25]
Antibacterial drugs	Stainless steel 304	1M HCl	5.10^{-4}M	90.5	[26]
galbanum (Ferula gummosa Boiss.) extract	Stainless steel 304	2M HCl	1000 ppm	90.72	[27]
Date Palm Waste extract	Stainless Steel 304	1M HCl	1.5g/L	91.09	This study
Silybum marianum leaves extract	Stainless Steel 304	1M HCl	1g/L	96.4	[28]

3.1.3. Electrochemical Impedance Spectroscopy (EIS)

The figure 4 shows the electrochemical impedance diagrams in the Nyquist Z plane, at different concentrations, carried out after 60 min of immersion at ambient temperature. The impedance spectrum has a form of a semicircle (a single capacitive loop), characterizing the formation of a double layer of capacitance Cdc. The impedance diagrams obtained have capacitive loops of different diameters; these patterns have a similar shape for all tested concentrations, indicating that, there is essentially no change in the corrosion mechanism [29]. These diagrams represented by the capacitive loops are generally associated with a mechanism of transfer of charges on an inhomogeneous surface [30]. When the concentration of the extract increased, we notice that the size of the capacitive loop increases: which can be attributed to the charge transfer process, this result suggests also the formation of protective film. The impedance spectra obtained are analysed in order to establish the equivalent circuit adapted to the experimental data.

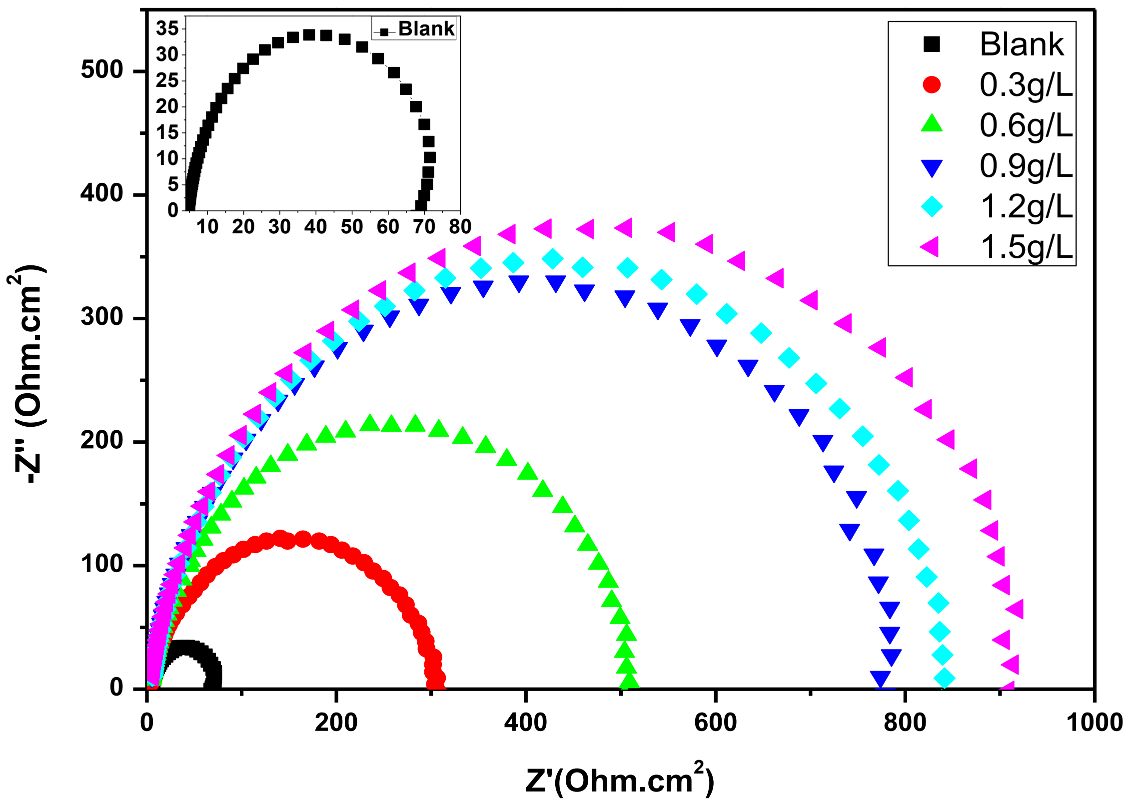

Figure 4. Nyquist plots for stainless steel electrode in 1M HCl solutions containing different concentrations of date palm waste at 25°C.

The equivalent circuit chosen to modulate the steel interface / solutions is shown in figure 5. This circuit is generally used to describe the metal / acid interface model [31]. With this model, and using the EC-Lab program, an excellent fit was obtained with the experimental data. The simulated spectrum from the CEE is almost super imposable to the experimental spectrum. The proposed circuit consists of an electrolyte resistor (Rs = R1), a constant phase element (CPE1) and a load transfer resistor (Rct = R2) which are in parallel. In general, a CPE (Qdl) is used in a model instead of a capacitor to account for the heterogeneity of the electrode surface resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption inhibitors and the formation of porous layers [31].

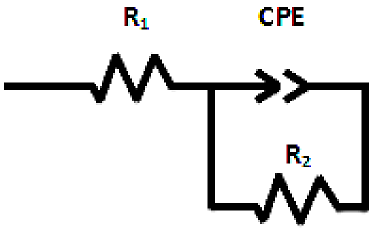

Figure 5. Equivalent circuits used to simulate the experimental results of the impedance curves EIS.

Table 3 shows the impedances parameters values, the Rct and inhibitory efficiency EI (%) values become larger with increasing concentration. Cdl double-layer capacitance values calculated in the presence of inhibitor are lower to that relative to blank solution; this decrease is associated with the adsorption of the inhibitory molecules on the surface of the steel. Indeed, more the inhibitor is adsorbed, more the thickness of organic deposited increases then the double layer capacity decreases according to his expression presented in the Helmotz model [32].

Table 3. Impedance parameters for 304 stainless steel in 1M HCl solutions in the presence and absence of date palm waste extract.

C extract (g L-1)	Rs (Ω.cm-2)	Rct (Ω.cm-2)	n	Cdl (µF.cm-2)	η_{EIS} (%)
Blank	4.910	112.87	0.992	104.72	---------
0.3	4.150	305.04	0.997	52.174	63.00
0.6	7.147	505.96	0.994	35.23	77.83
0.9	7.103	795.08	0.995	26.85	85.80
1.2	5.887	850.97	0.996	26.37	86.74
1.5	5.489	936.46	0.994	25.22	88.03

3.2. Surface analysis

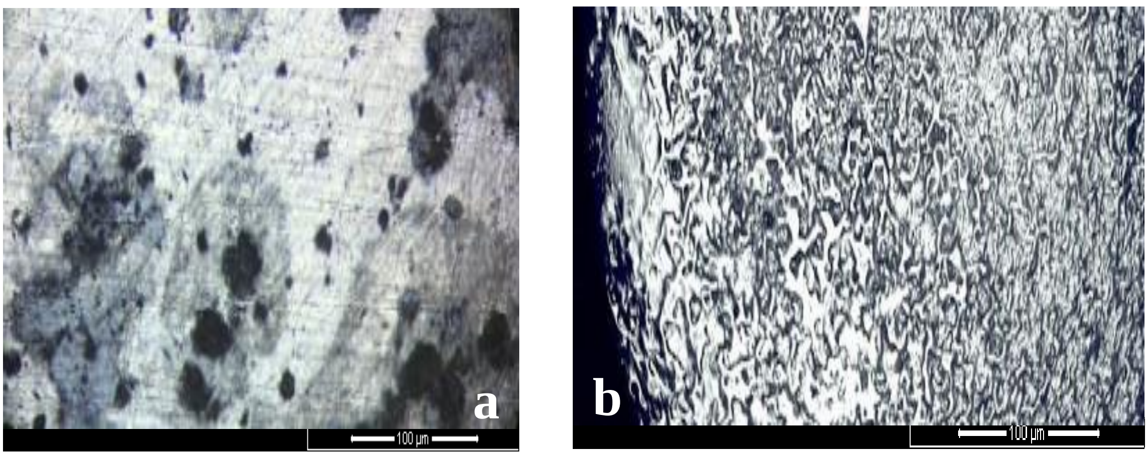

Figure 6. Image observed with the metallographic microscope of 304 stainless steel specimen (a) after 24 h immersion in blank 1M HCl solution, (b) after 24 h immersion in 1M HCl solution containing 1.5 g L-1 of the extract.

In order to confirm the inhibitory character of our extract, microscopic surface images of 304 stainless steel were taken in the absence and the presence of 1.5 g / l of the extract. The figure 6a shows that the surface of the steel is very porous; holes of various diameters appear at the surface, which confirms the damage of the steel in the absence of the extract. The steel surface in figure 6b shows less damage and a protective film are visualized when the extract has been added to the corrosive medium, which confirms the protection provided by the extract and the reduction of the corrosion rate.

3.3. FTIR spectrophotometry

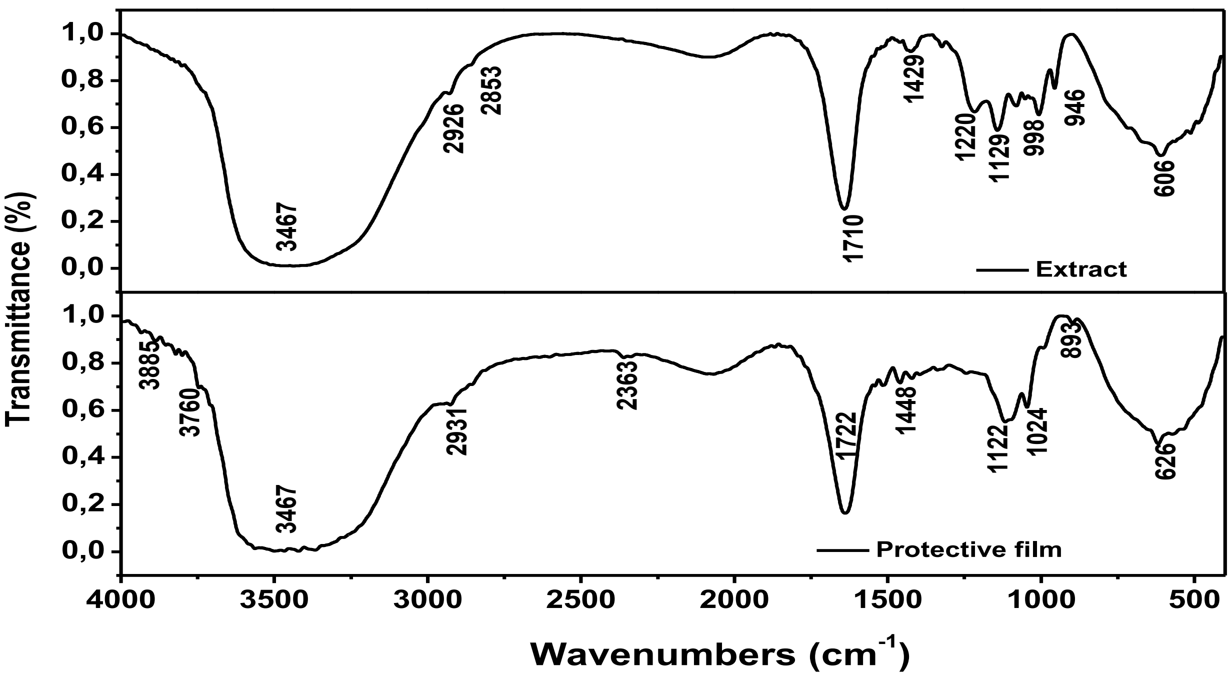

Figure 7. The FT-IR spectra of date palm waste extract and corrosion product.

The date palm extract and the product, adsorbed to the surface of the steel, were analysed by infrared spectroscopy. Figure 7 shows the spectra of these two products, from 7a, we can predict the existence of hydroxyl O-H groups attributed at 3467 cm^{-1}, the low bonds at 2926 cm^{-1} and 2853 cm^{-1} indicate the presence of the aliphatic and aromatic C-H groups, respectively [33, 34]. The bonds appeared at 1710 cm^{-1}, 1429 cm^{-1} and 1129 is attributed to the carbonyl group, C–H bending in $–CH_2$ and C-O stretching vibration respectively, the rest of the characteristic bonds appear at frequencies less than 998 cm^{-1} are assigned to the vibration of C-H bond. Infrared spectrum of the protective film indicate the presence of some bonds similar to the spectrum of the extract with a slight displacement of appropriate frequencies. According to this spectrum we note the appearance of low bonds at 3885 cm^{-1} and 3760 cm^{-1} probably attributed to the Fe-O bond [34], which confirms the adsorption of the extract at the surface of the electrode. The frequencies at 3467 cm^{-1}, 2931 cm^{-1} and 1722 cm^{-1} are attributed respectively to the O–H, C–H bonds and the carbonyl groups, the passage of their wavenumber to higher values, is explained by the formation of Fe-extracted complex at the surface metal [35].

4. CONCLUSION

From the experimental results found in this study, the following conclusions can be drawn:

- The inhibition efficiency of 304 stainless steel in 1M HCl medium increases with increasing concentration of the extract, a value of 91% was calculated when 1.5g / L of the extract was added.
- The extract act as a mixed-type inhibitor with an anodic predominance.
- The corrosion is controlled by charge transfer process, the addition of extract at the corrosive solution increase Rt values while reduces Cdl values.
- The inhibition is due to the adsorption of the extract molecular at the metal surface then blocking its active sites by the formation of Fe–inhibitor complex, takes place at the pores of oxide layer.

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