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Effect of Dates Extracts as Environmentally Friendly Corrosion Inhibitor for Carbon Steel in 1M HCl Solution

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Abstract- Inhibitory effect of extracts from three date varieties namely khalt (kha), Lassiane (La) and Tadmamt (Td)), and the mixture of date varieties as environmentally friendly corrosion inhibitor for carbon steel in 1M HCl is studied by means of electrochemical tests such as electrochemical impedance spectroscopy (EIS), and Tafel polarization. It's been obtained that in 1.0 M HCl solution the date extracts are a new green corrosion inhibitor for carbon steel. The results found show that with increasing concentration of the date extracts the values of inhibition efficiency increased. Comparison of the experimental results of the three varieties and the extract mixture of dates, exhibited that inhibition efficiency increased in order Kha, La, Td and the mixture. Therefore, the extract mixture is the best inhibitor with a maximum inhibitory efficacy value reaching 91% at a concentration of 1% of the mixture. Polarization study revealed that dates extracts acted as a mixed inhibitor, with more principally cathodic process. The compounds of the date extracts are adsorbed on the metal surface forming the protective film, which explains the inhibitory action of these extracts, this result is confirmed by electron scanning microscopy (SEM).

Keywords- Green inhibitor; electrochemical tests; electron scanning microscopy (SEM)

1. INTRODUCTION

Corrosion producing changes in the chemical properties of the material, is a degradation of the physical properties of materials [1-2], it affects many areas, in particular metallic materials. Corrosion is a major problem for our industrial civilizations for several reasons. Its economic impact, given the cost of damage and equipment replacement [3–5]. On the other hand, the direct or indirect consequences of corrosion can have a lasting impact on our environment and our health.

The protection of corrosion by using the inhibitors is considered a better technique for prevent or stop the degradation of metals and alloys in the industry [6]. In order to preserve the environment and the issue of toxicity, the researchers ordered their studies to use green corrosion inhibitors instead of certain synthetic inhibitors [7–9].

Plant extracts and essential oils are usually as ecological corrosion inhibitors because they are biodegradable, economic, simple to handle and easy to extract [3–5,10–12]. These benefits have led researchers to study natural materials as green corrosion inhibitors for various corrosive environments such as Chamomile Oils [13], Santolina pectinate oil [14], Cystoseira Gibraltarica Extract [15], Senecio anteuphorbium [16], Oil of *J.* Juniperus Phoenicea [17], Ceratonia Siliqua L Oil [18], Mentha pulegium oil [19], Curcumine Longa [20], Thymus satureioides oil [21]. The inhibitory effect of plant extracts is demonstrated by its richness in alkaloids, tannins and amino acids [14] and organic components such as oxygenated monoterpenes, sesquiterpenes, and hydrocarbons [22].

According to previous research which shows the anti-corrosive effect of the date palm on an aluminum alloy in the NaCl solution at 3.5% [23], we are interested in the effect of extracting Moroccan date varieties as an ecological inhibitor of corrosion of carbon steel in the corrosive solution of 1M HCl.

The main objective of this work is to know the effect of the inhibition and inhibitory action of date extract as a green corrosion inhibitor for carbon steel in hydrochloric acid 1M, using electrochemical measurements of potentiodynamic polarization and impregnable electrochemical spectroscopy impedance and by analyzing the morphology of the steel surface using a scanning electron microscope.

2. MATERIALS AND METHODS

2.1. Preparation of extracts

The dates used in this work were isolated from three Moroccan date palm fruits; khalt (kha), Lassiane (La) and Tadmamt (Td), She's been picked up at the full maturity “Tamr stage”, the mixture of these varieties of Moroccan dates also analyzed. Before extraction, the fruits of each variety were washed separately, well dried and then ground and sifted into powder.

Oil extraction was done exhaustively with petroleum ether by a Soxhlet for 8 hours between 313 and 333 K [24]. The solvent was evaporated to 313 K with the help of a rotating evaporator, then these oils stored in a freezer at 277 K until the analysis [25].

2.2. Materials and solutions

The corrosive solution of HCl 1M was obtained by dilution of the concentrated analytical hydrochloric acid solution with a percentage of 37% HCl using distilled water and the molarity is checked by acid-base determination with NaOH, The inhibition concentration ranges used are from 0.001% to 1% of the extract.

All corrosion examinations were conducted on carbon steel specimens with the next weight inches chemical composition: C (0.07%), Mn (0.19%), Si (0.03%), Cr (0.05%), Al (0.02%) and Fe the rest. Before each test, the carbon steel specimens used were polished with different qualities of abrasive paper from 180 to 1200 gravel. Then the samples were carefully rinsed with distilled water, and then cleaned with acetone.

2.3. Electrochemical experiment

For all electrochemical tests, we used a 100-type controlled Potentiostat OrigaStat with analysis software (OrigaMaster). The corrosion cell used is equipped with three electrodes, a saturated calomel electrode being a reference electrode, and the auxiliary electrode used was platinum. The carbon steel plate is used as a working electrode a surface of 1 cm^2. The working electrode was first put into the open circuit test solution (OCP) for 30 minutes until it reached a stable state to establish the value of (E_{ocp}).

The measurements of electrochemical impedance spectroscopy (EIS) were performed at OCP in frequency from 1 kHz to 100 mHz with the use of a voltage of 5 mV of ac sine wave. The impedance diagrams have been converted into Nyquist representation. After the measurements (EIS), measurements of potentiodynamic Tafel were made with a scanning rate of 20 $mV.s^{-1}$ of cathode at anodic direction, from -750 to -100 mV. The temperature is controlled during all analyses.

2.4. Surface analysis

Before each measurement, the specimens of carbon steel were mechanically polished and rinsed with acetone and dried with lime air. After a 24-hour immersion in the HCl 1M solution without and with 1% of dates extract at 298 K.

Surface analysis of carbon steel samples was examined with a Scanning Electron Microscopy SEM type: JSM-IT10.

3. RESULTS AND DISCUSSION

3.1. Electrochemical experiments

3.1.1. Potentiodynamic polarization curves

The Figs 1.2.3.4 illustrates the potentiodynamic polarization curves for carbon steel electrodes in 1 M HCl at 298 K without and in with addition of different concentrations of the extract of dates.

Table 1. Polarization parameters for carbon steel in the presence and absence of dates extract (Kha, La, Td) and the mixture in 1 M HCl at 298 K

	C	E_{corr}(mV)	i_{corr}(mA/cm^2)	B_c(mV)	B_a(mV)	E_I (%)
HCl	1M	- 513.7	0.193	-104	113.8	-
Kha	0.00 1%	- 537.2	0.088	-129	78	54.7
	0.01 %	-535.6	0.102	-145	83	47.1
	0.1 %	-534.2	0.079	-104	72	59.1
	1 %	-516.4	0.041	-66	55	79.3
La	0.00 1%	-533.7	0.082	-142	73	57.6
	0.01 %	-552.7	0.060	-141	47	86.9
	0.1 %	-549.2	0.053	-141	47	72.5
	1 %	-534.3	0.039	-93	70	79.9
Td	0.00 1%	-547.0	0.084	-120	73	54.6
	0.01 %	-595.4	0.068	-111	69	64.7
	0.1 %	-533.3	0.056	-101	75	68.9
	1 %	-543.7	0.036	-76	99	81.6
The mixture	0.00 1%	-541.2	0.053	-94	71	72.5
	0.01 %	-522.6	0.055	-81	59	71.3
	0.1 %	-524.4	0.055	-85	60	71.4
	1 %	-519.3	0,017	-63	62	91.3

Table 1 presents the various electrochemical parameters, as well as (i_{corr}) corrosion current density, (E_{corr}) corrosion potential, and (b_a, b_c) Tafel's cathode and anodic slopes, which are obtained from the extrapolation of i-E polarization curves.

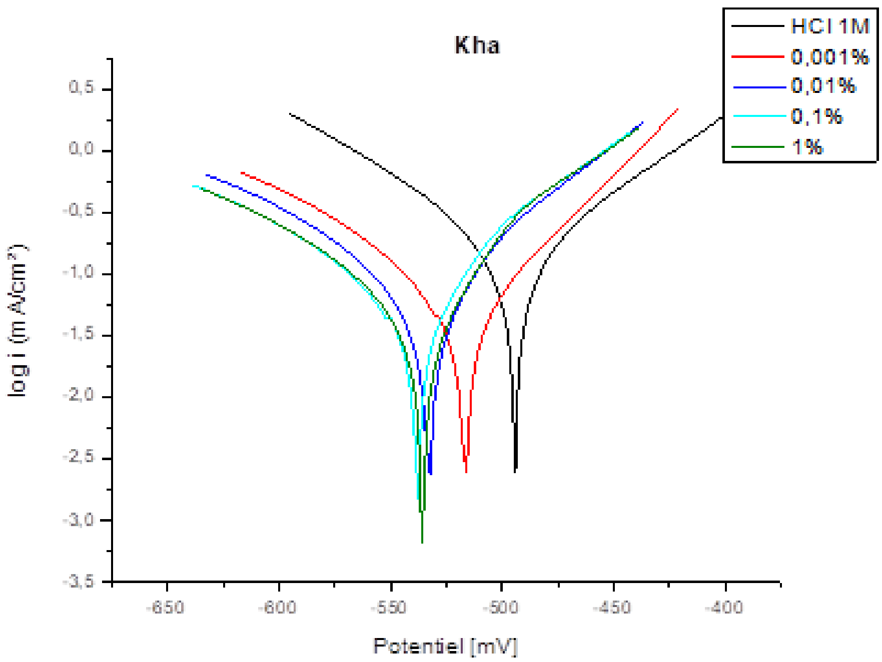

Fig. 1. Polarization curves of carbon steel with the addition of different concentrations of Kha in HCl 1M at 298 K

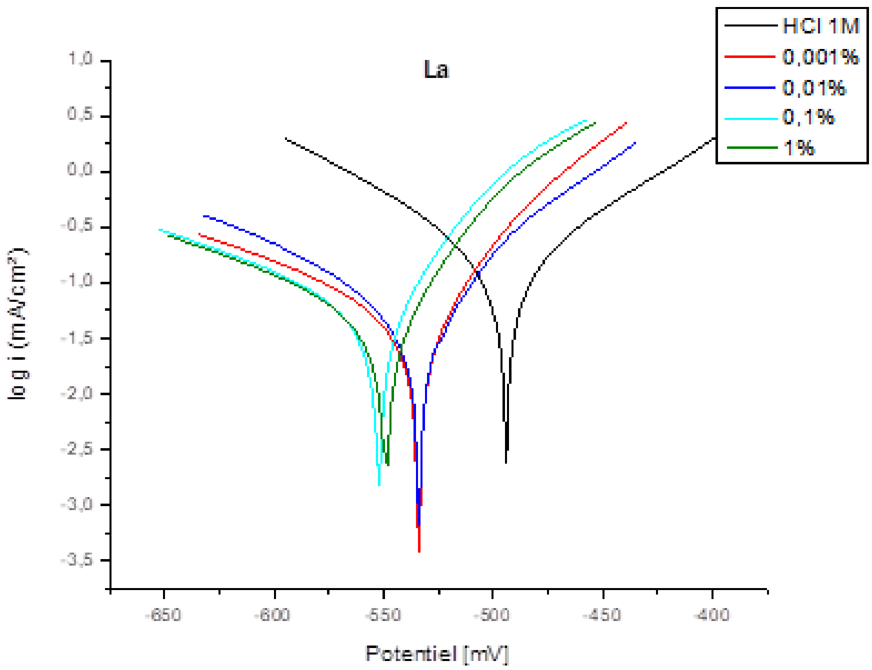

Fig. 2. Polarization curves of carbon steel with the addition of different concentrations of La in HCl 1M at 298 K

Also values the inhibition efficiency E_I (%) are listed via equation (1) [26]:

$$\boldsymbol{E_I}(\%) = \frac{\boldsymbol{i_{corr}} - \boldsymbol{i_{corr}}/_{\boldsymbol{inh}}}{\boldsymbol{i_{corr}}} \times \mathbf{100} \quad (1)$$

where i_{corr} and $i_{corr/inh}$ are the values of current densities without and with dates extracts respectively.

Table 1 shows that the values of i_{corr} decreased with increased concentration of extracts from the three varieties of dates and mixing. also, E_I(%) increases with increased concentration of inhibitors in 1M HCL. inhibition efficiency expects 79.3%, 79.9%, 81.6% and 91.3% for Kha, La, Td, the mixture respectively.

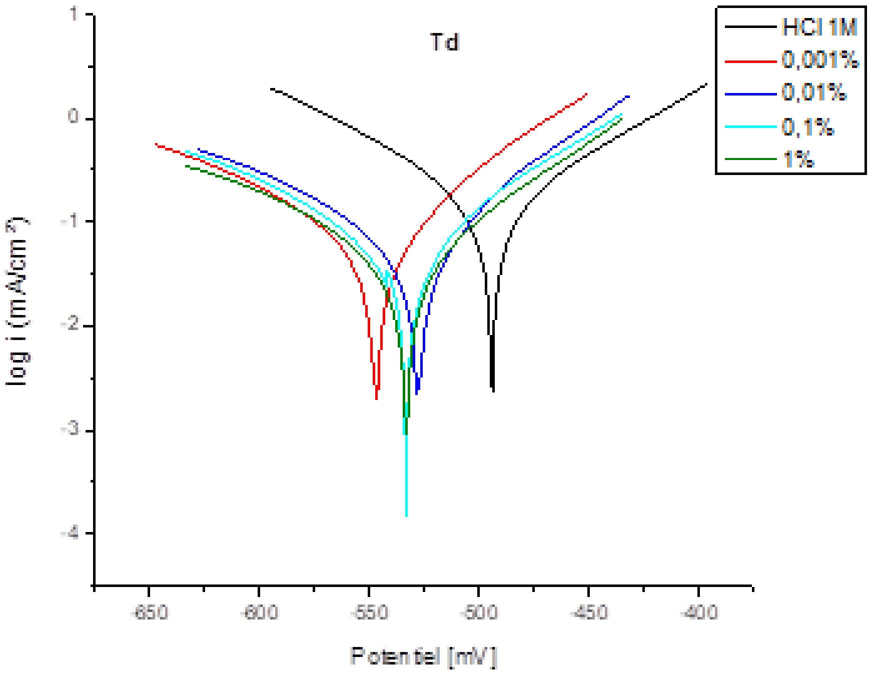

Fig. 3. Polarization curves of carbon steel with the addition of different concentrations of Td in HCl 1M at 298 K

Figs 1.2.3.4 presents polarization curves moving to lower current densities with increased date extract concentration for all varieties as well as mixing, consequential in a decrease in carbon steel corrosion rates. The cathode portion of the polarization curves of the extracts of the three dates varieties, there is a shift of corrosion potentials to negative values in relation to white. This indicates that the cathode reaction of the corrosion process is repressed and thus protects the steel from corrosion. Therefore, the results showed that the extract of dates acts as mixed type inhibitors, but more predominantly cathodic process [27,28].

Table 1 shows that the values of (i_{corr}) decrease with the presence of dated extract, and with the increase in concentration of these extracts. The inhibitory efficacy values for the three varieties of dates extract at to each concentration are high, and expect maximum values of 91.3% for the mixture at concentrations of 1%. These results designate that there is a protective film formed about the surface of carbon stell [28,29].

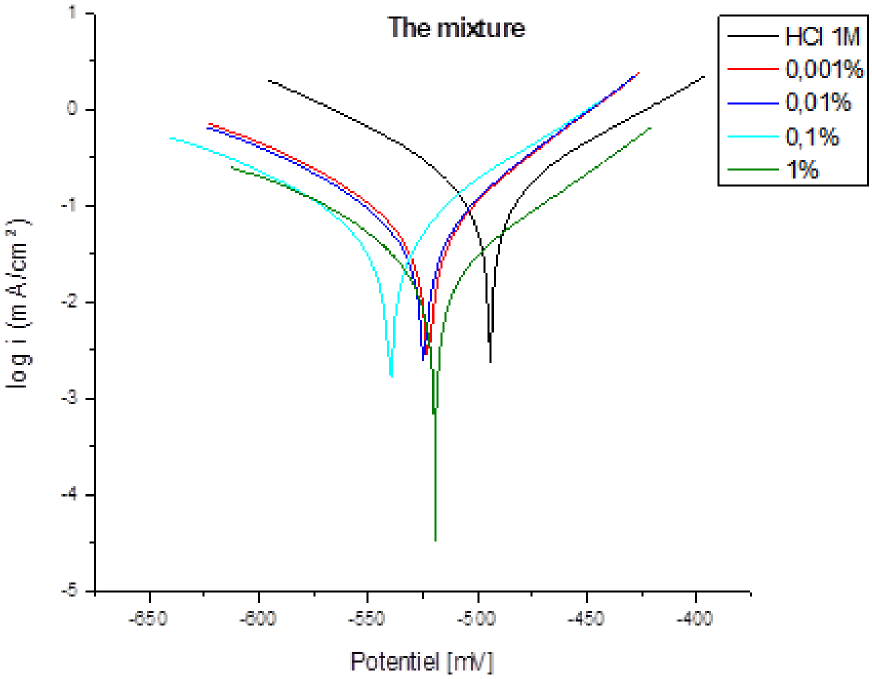

Fig. 4. Polarization curves of carbon steel with the addition of different concentrations of the mixture in HCl 1M at 298 K

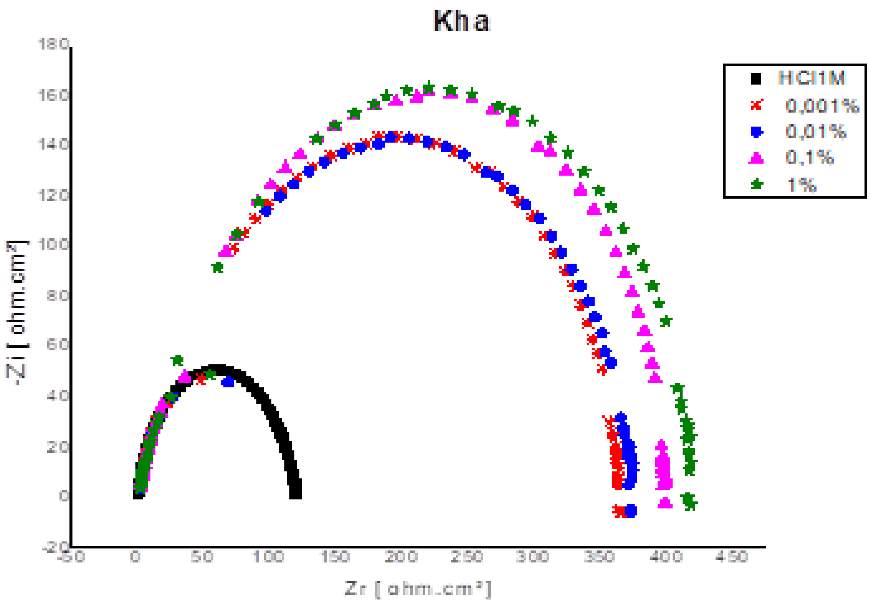

Fig. 5. Nyquist plots of carbon steel without and with diverse concentrations of Kha in 1 M HCl at 298 °K (immersion time 30 min)

3.1.2. Electrochemical impedance studies

Figs. 5,6,7,8 illustrate the Nyquist diagrams of carbon steel after 30 minutes of immersion in the absence and presence of different inhibitor concentrations in HCl 1M. Table 2 shows electrochemical parameters for example load transfer resistance (R_t), solution resistance (R_s)

and double-layer capacity (C_{dl}) that are given from Nyquist plots [30]. Inhibition efficiency (E_R) is calculated by using equation (2) [31,32]:

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

where R_t^0 and R_t are charge transfer resistances in the absence and in the presence of the dates extracts respectively.

Table 2. EIS parameters for the corrosion of carbon steel in 1 M HCl without and with addition of diverse concentrations of dates extracts (Kha, La, Td) and the mixture at 298 °K

	C	C_{dl}(µF.Cm^{-2})	R_s (Ω.Cm^2)	R_t(Ω.Cm^2)	E_R (%)
HCl	1M	133.6	0.15	119	-
Kha	0.00 1%	116.8	2.15	365	67.4
	0.01 %	114.6	2.25	372	68.0
	0.1 %	93.0	2.55	397	70.0
	1 %	125.2	2.31	418	71.4
La	0.00 1%	237.1	2.83	336	64.5
	0.01 %	167.2	3.22	425	72.0
	0.1 %	184.6	3.17	439	72.9
	1 %	93.6	2.15	537	77.8
Td	0.00 1%	175.0	1.55	334	64.4
	0.01 %	124.2	1.45	421	71.7
	0.1 %	121.3	2.75	467	74.5
	1 %	59.4	2.58	539	77.9
The mixture	0.00 1%	120.6	1.96	366	67.4
	0.01 %	121.8	2.19	392	69.6
	0.1 %	85.8	2.54	416	71.4
	1 %	28.6	4.55	1415	91.5

Fig. 2 shows that impedance plots have depressed semicircles for all date extracts tested; showing that corrosion of carbon steel is controlled by load transfer [33]. And with increased concentration of the extract from dates, the diameter of the semi-circles grows. EIS results show that inhibition efficacy (E_R%) increases with increased concentrations, as well as R_t

values increase while C_{dl} values decrease with the addition of dated extract. The increase in R_t values is explained by the diminution in the local dielectric constant and/or the rise in the thickness of the double electrical layer. which leads to the formation of a protective film on the steel surface [34,35]. The decrease in the values of dual-layer capacity is attributed to the regular replacement of the water molecules by the inhibitor molecules used [1].

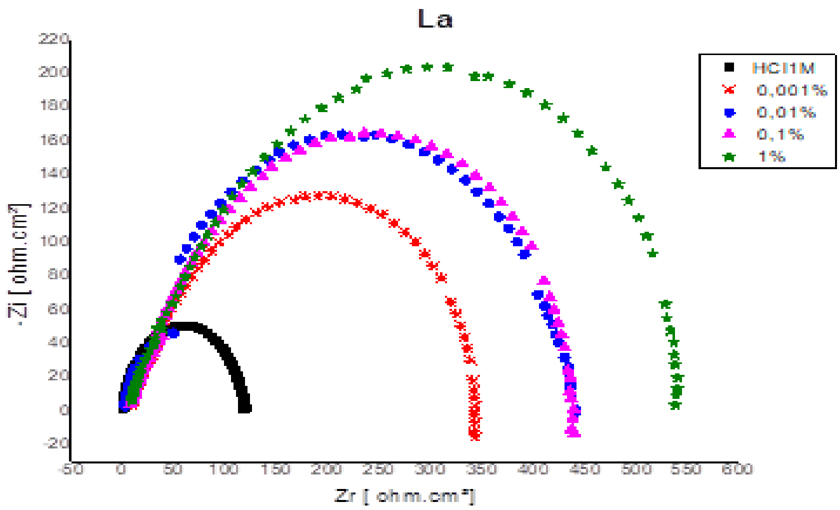

Fig. 6. Nyquist plots of carbon steel without and with diverse concentrations of La in 1 M HCl at 298 °K (immersion time 30 min)

These results confirm that the effectiveness of inhibition increases with the increase in inhibitory concentration and reach 71.4% for Kha, 77.8% for Td, 77.9% for La, and 91.5% for the mixture for 1% of extract concentration.

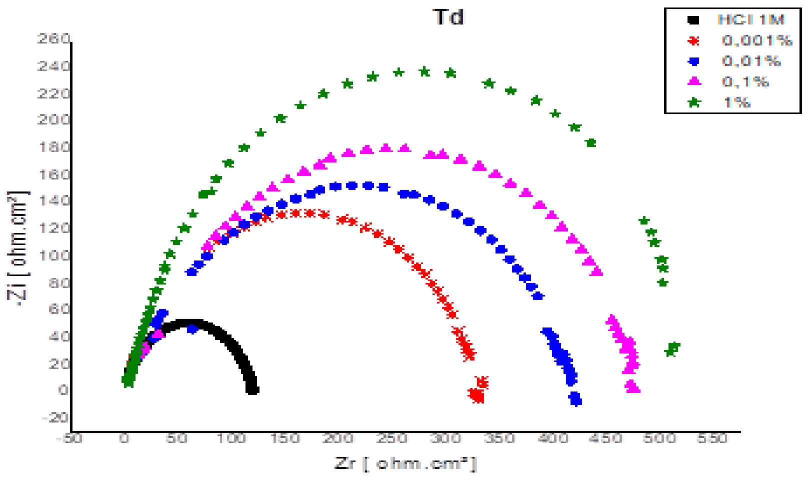

Fig. 7. Nyquist plots of carbon steel without and with addition of diverse concentrations of Td in HCl 1 M at 298 °K (immersion time 30 min)

This shows that these extracts are good corrosion inhibitors for carbon steel in 1M HCl.

These results are in good agreement with those obtained from polarization measures. And by comparing the three varieties and the extract mixture of dates, it turns out that the blending of extracts has the best efficacy as corrosion protection with an efficiency of 91,5%.

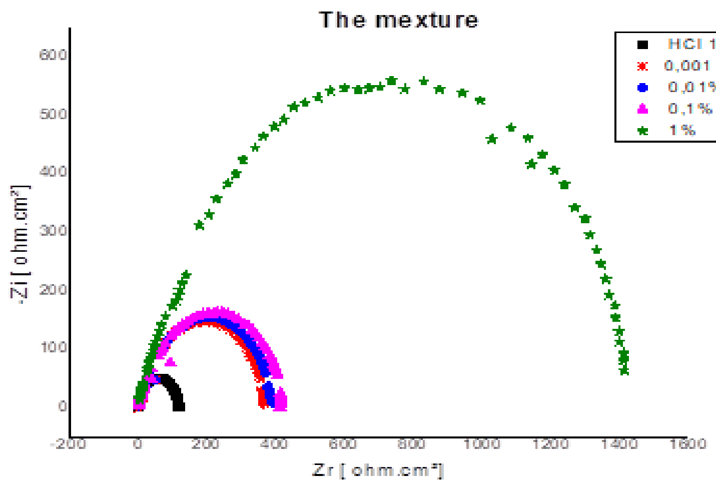

Fig. 8. Nyquist plots of carbon steel without and with diverse concentrations of the mixture in 1 M HCl at 298 °K (immersion time 30 min)

3.2. Surface analysis

The morphology by the SEM photos was carried in HCl only and in the presence of 1% of the three dates extracts and the mixture. Fig. 9 gives the morphology of corrosion products created after 24 hours of immersion on the surface of the steel in the corrosive solution HCl 1M with and without inhibitors.

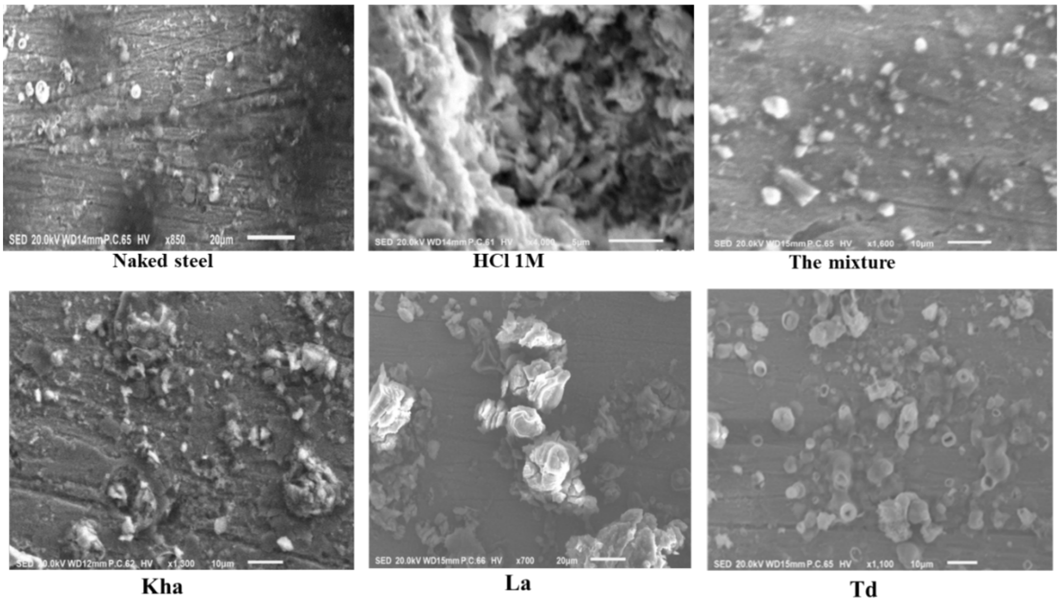

Fig. 9. SEM analysis of the carbon steel in without and with addition of 1% of dates extracts in 1M HCl solution

It is clear that there is the formation of a porous surface as a result of the corrosion process. In the presence of 1% of Kha, La, and Td dates extract and 1% of mixture, caused in the formation of an inhibitory film that has the role of a barrier between steel and the corrosive environment, which subsequently prevents corrosion reactions of anodic oxidation of iron and cathodic reduction of hydrogen [36]. This difference in morphology without and with inhibitors may also have affected corrosion resistance [37].

4. CONCLUSION

The inhibition of corrosion of carbon steel in the medium 1M HCl was achieved using dates extracts as eco-friendly corrosion inhibitors. In summary of this work, results from electrochemical analyses of EIS and PDP showed that the efficiency of corrosion inhibition increased with an increase inhibitor concentration. The highest inhibition efficiency is 1% of concentration for the extracts dates variety. Comparison of the experimental results of the three varieties and the extract mixture of dates, showed that inhibition efficiency increased in order Kha, La, Td and the mixture. Therefore, mixing extracts is the best inhibitor. The Potentiodynamic polarization measures have shown that extracts from dates act as mixed-type inhibitors, with more dominant cathodic process. The analysis of morphology by SEM in the presence of date extract confirmed the formation of a protective film on the surface of the steel confirmed the formation of a protective film on the surface of the steel in the presence of the extract of dates.

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