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Effect of Methanol Extract of Chamaerops Humilis L. leaves (MECHLL) on the Protection Performance of Oxide Film Formed on Reinforcement Steel Surface in Concrete Simulated Pore Solution

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The methanol extract of Chamaerops humilis L. leaves (MECHLL) obtained by the soxhlet technique was analyzed by GC/MS and FT-IR spectroscopy. The extract is constituted by Lucenin 2 (42%), Dasycarpidan-1-methanol, acetate (ester) (11%), 1, 3-D-5-hexan-2-one-2, 4-dinitrophenylhydrazone (10%) and 9-Hexadecenoic acid (8%) as the most abundant compounds. The effect of the extract on the protective property of the oxide film formed on the reinforcement steel surface in alkaline solution (pH > 13) was investigated by electrochemical techniques. Inhibition efficiency of 42% was obtained with 0,5g/L of inhibitor at 25°C.The Nyquist plots showed that the variation of immersion time increases the polarization resistance and associated capacitance. The addition of the inhibitor can effectively decrease the reinforcement steel corrosion, enhance the stability of the film formed in alkaline solution and lead to the formation of a more compact protective layer on the surface. Action of the MECHLL obeys to the Langmuir adsorption isotherm. Finally the inhibition efficiency of the extract was discussed in terms of adsorption and protective film formation.

Keywords: Concrete simulated pore solution, Chamaerops humilis L., Reinforcement steel, Oxide film, corrosion, inhibition.

1. INTRODUCTION

Concrete is very particular medium that is characterized by different phases, including an interstitial electrolyte. This electrolyte is essentially a Ca $(OH)_2$ saturated solution, containing significant amounts of KOH and NaOH [1]. In the high alkaline (pH>13) environment provided by concrete, steel rebar is protected against corrosion by a passive oxide film [2-4]. This protective film is strongly adherent and chemically stable in alkaline conditions [5].

Over the years a number of protection measurements have been suggested by many workers to delay, slow, or stop the corrosion process, thereby enhancing the service life of concrete structures. One of the practical methods suggested for control of steel corrosion in concrete is the use of corrosion inhibitors [6].

Two approaches are generally used to evaluate the efficiency of inhibitors for this application, one uses simulated pore solution testing, and the other uses actual concrete or mortar specimens. Both methods are sometimes used in conjunction [7].

Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors; they are the riche sources of ingredients which have very high inhibition efficiency (I.E) [8]. Several studies showed that for low concentrations of the inhibitor the inhibition efficiency was able to exceed 90% [9-16], but El-Etre and all, explained that the degree of inhibition depends on the nature of metal and the type of the medium. they demonstrate that inhibition efficiency of lawsonia extract a 800 ppm for C-steel, decreases with pH solution, alkaline (69,56%) < neutral (91,01%) < Acid (95,78%) [17]. Researches generally agreed that most of these plant extract are green corrosion inhibitor because they are biodegradable, less toxic and do not contain heavy metals [18].

Chamaerops humilis L. is a medicinal plant which belongs to the Arecaceae family. It is frequently found in the North Africa especially occidental mediterranean area. Chamaerops humilis can grow up between 1 to 1.5 m in mean height. But, this plant can reach 9 to 10 m of height in the protected areas. In literature the phytochemical analysis of methanol leaves extract reveal the presence of Gallic Tannins, Saponins, Flavonoids, Terpenoids and Anthacenosides [19].

In the present work, the performance of the passive film and the inhibiting efficiency of the MECHLL against the corrosion of reinforcement steel were investigated in concrete simulated pore solution. The study was performed using GC-MS, FT-IR and electrochemical techniques.

2. EXPERIMENTAL PART

2.1 Materials

2.1.1 Preparation of plant extract

Chamaerops humilis L. plant was collected in October 2010 in the region of Bensliman, Morocco.

Chamaerops humilis L. leaves were air-dried ten days in the laboratory at room temperature, before their uses for the preparation of the extract. The extraction was realized by the soxhlet technique during (6 hr) with the methanol as solvent of extraction. The extracted solution was concentrated until extract solidification. This solid extract was used to study the corrosion inhibition. It was dissolved in

0,1M NaOH+ 0,5M KOH at different concentrations ranging from 0,3g/l to 1g/l. The solution testes are freshly prepared before each experiment.

2.1.2 Analysis and characterization of extract techniques.

The chemical composition of the extract was analyzed using a gas chromatograph (Trace GC ULTRA) equipped with a capillary column VB-5 (5% phenyl-polymethylsiloxane, 30 m length; 0,25 mm i.d.; 0,25 µm film thickness) and coupled to a mass selective detector (Polaris Q MS type trappe ionique). Helium was used as the carrier gas at a flow rate 1.5 ml/min. The injector, used in the split mode, and detector temperature were 220 and 300°C respectively, oven temperature programmed from 70 to 300°C at 10°C/min. Isothermal temperature was at 300°C for 15 min. EI mass spectra were collected at 70 eV. The ion source temperature was set at 200°C. Identification of components was assigned by matching their mass spectra with the NIST/EPA/NIH Mass Spectral Library Version 2.0 (2002). The quantity of all identified components was investigated by using a percent relative peak area as shown in Table 1.

The plant extract (coated on KBr disc) was also characterized by FT-IR spectroscopy (VERTEX 70 FT-IR). Spectrum was obtained at 4cm^{-1} resolution and 20 scans.

2.1.3 Sample Preparation.

The chemical composition of reinforcement steel (R.S) (wt. %), is reported in the table 1.

Table 1. Chemical composition of reinforcement steel.

Elements	C	Mg	Si	P	Mn	S	Cu	Fe
Wt.%	2.81	0.87	0.45	0.33	1.34	0.31	1.29	balance

The sample was used as working electrode, consisting of R.S disc axially embedded in a Teflon holder to offer of flat disc shaped surface of 0,158 cm^2 area. The exposed area was mechanically polished with 400, 600, 1200 and 1500 grades of Abrasive papers, rinsed by distilled water and degreased with acetone before each electrochemical experiment.

2.1.4 Electrolyte

The measurements were carried out in 0,1M NaOH+ 0,5M KOH solution, pH ≈ 13,2 prepared with grade chemical reagents and distilled water. The measured pH was 13,2 this solution was chosen in order to simulate the pH of concrete pore solution, all the test were performed at room temperature (25°C).

2.2 Electrochemical measurements

Electrochemical study, including Chronoamperometry measurements, Open Circuit potential measurements, and electrochemical impedance spectroscopy (EIS), were carried out by a PGZ 301 potentiostat (Radiometer Analytical), monitored by voltamaster 4 software.

Each experiment was repeated three times to confirm reproducibility of the results. AC potentials are reported to Ag/ AgCl reference electrode.

3. RESULTS AND DISCUSSION

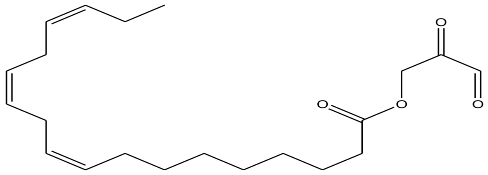
3.1 Characterization of plant extract

3.1.1 GC-MS study

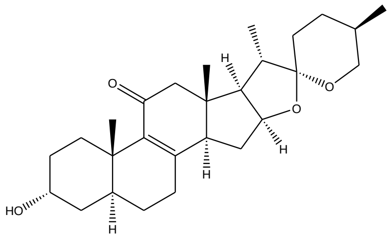
Gas chromatography (GC)–mass spectroscopy (MS) spectra of dried plant extract allowed the identification of 12 compounds. It contains 7 major peaks along with many small peaks indicating presence of more than 12 major compounds. The retention times (RT), the compounds and the peak area are reported in table 2.Since (RT) of majority of compounds is close to each other and it is very difficult to separate them, the methanol extract of Chamaerops Humilis L. was used for corrosion inhibition studies.

Table 2. GC-MS characterization of the main constituents of MECHLL.

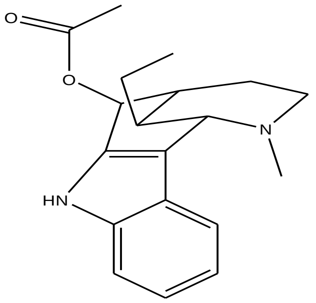
RT (mn)	Compound	Peak area (%)
14.67	9-Hexadecenoic acid	7.85
16.34	1,3-D-5-hexan-2-one-2,4-dinitrophenylhydrazone	10.15
16.97	Dasycarpidan-1-methanol, acetate (ester)	11.14
19.42	9,12,15-octadecatrienoic acid, 2,3-bisoxypropyl ester, (z,z,z)-	3.13
27.32	Spirost-8-en-11-one, 3-hydroxy-, (3a,5a,14a,20a,22a,25R)	4.28
28.25	Lucenin 2	42.29
29.85	Glycine,N-[(3a,5a,7a,12a)-24-oxo-3,7,12-trioxycholan-24-yl]-, methyl ester	3.26



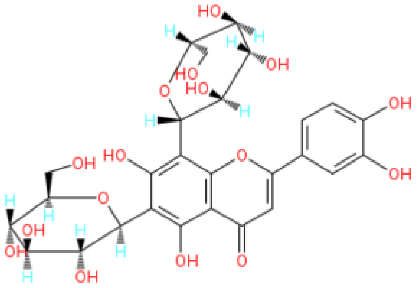
[9, 12, 15-octadecatrienoic acid, 2, 3-bisoxypropyl ester, (z,z,z)]



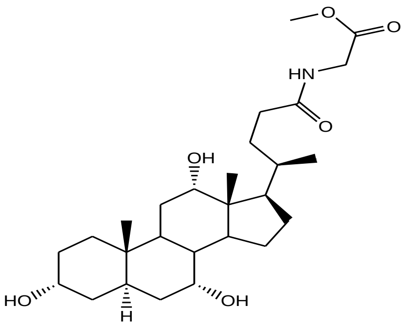
[Spirost-8-en-11-one, 3-hydroxy-, (3a, 5a, 14a, 20a, 22a, 25R)]



[Dasycarpidan-1-methanol, acetate (ester)]



[Lucenin 2 (Luteolin 6,8-di-*C*-glucoside)]



[Glycine, N-[(3a, 5a, 7a, 12a)-24-oxo-3, 7, 12-trioxycholan-24-yl]-, methyl ester]

Figure 1. Chemical structures of some compounds identified in GC-MS spectrum of MECHLL.

3.1.2 FT-IR study

FT-IR spectrum of methanol extract of Chamaerops Humilis L. leaves is shown in Figure 2.

The FT-IR shows strong adsorption at 3352.6 cm^{-1} can be attributed to alcohol function OH. The band 1609 cm^{-1} corresponds to N-H. The peaks at 1518.4 cm^{-1} and 1443.9 cm^{-1} can be attributed to (C=N) or the aromatic ring (C=C) (the presence of the phenol). The oscillations at 1383 cm^{-1} present two strong bands (NO_2). The adsorption at 1281.8, 1176.7 and 1073.8 cm^{-1} can be attributed to the acid function, the tertiary alcohol and primary alcohol, respectively. The peaks at 1408 cm^{-1} corresponding ether group (RO-) to the 1015.4 cm^{-1} can be attributed to a secondary alcohol and unsaturated substituted. Finally the low frequency bands (900.1 and 848 cm^{-1}) correspond to C-H function.

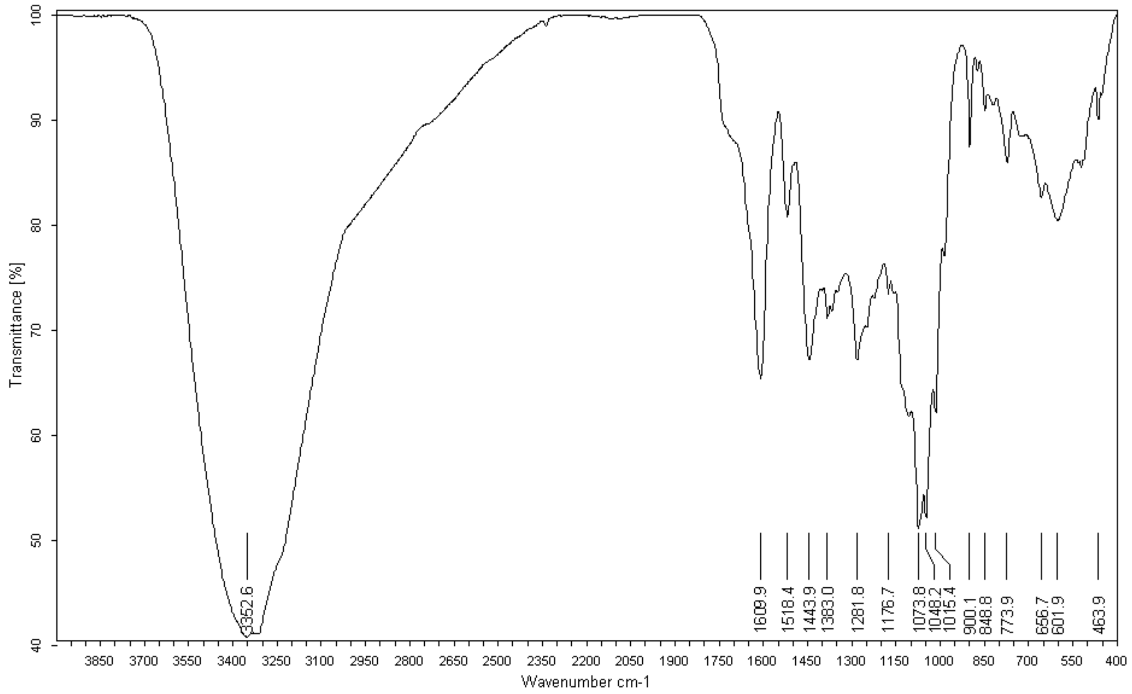


Figure 2. FT-IR spectrum of MECHLL.

The results obtained by GC-MS and FT-IR indicate that MECHLL is rich in molecules that contain heteroatoms such as (O and N). According to the literature, these compounds can be used as corrosion inhibitor, because the heteroatoms are able to establish a link between inhibitor and several metals area. Thus in the following part, we are going to test this extract in concrete simulated pore solution using various electrochemical techniques. Interpretation of results allows to understand the inhibitor behavior toward the protective layer of the metal in this environment.

3.2 Open circuit potential (OCP) measurements

To show the influence of chamaerops humilis L. leaves extract on steel corrosion in simulated concrete pore solution, experiments were carried out for 3 hours immersion at pH ≈ 13,2 in two different solutions. The first solution contained 0, 1 M NaOH + 0,5 M KOH and the second 0,1 M NaOH+ 0,5 M KOH+ 0,5 g/L of the extract (Figure 3).

It is clear that the evolution of the OCP in registered by the negative values after the immersion of the R.S in both solutions. And after we notice a fast evolution with immersion time of the potential towards nobler values according.

The stability of the potential (E= -337 mV) can be explained by the formation of oxide layer [20, 21]. The addition of the inhibitor, the continuous evolution of potential to the anodic direction (E= -317 mV) is observed, this can be attributed to the spontaneous adsorption of inhibitor on electrode surface.

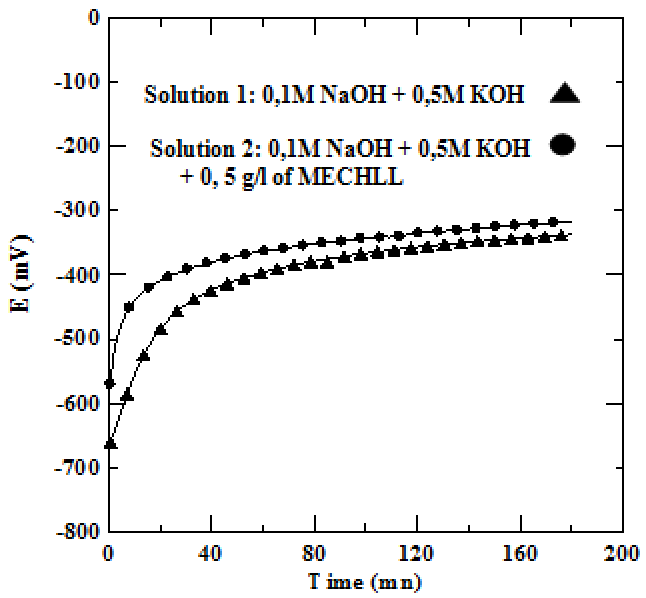


Figure 3. Evolution of Open circuit Potentials electrode in different solutions.

3.3 Chronoamperometry measurements

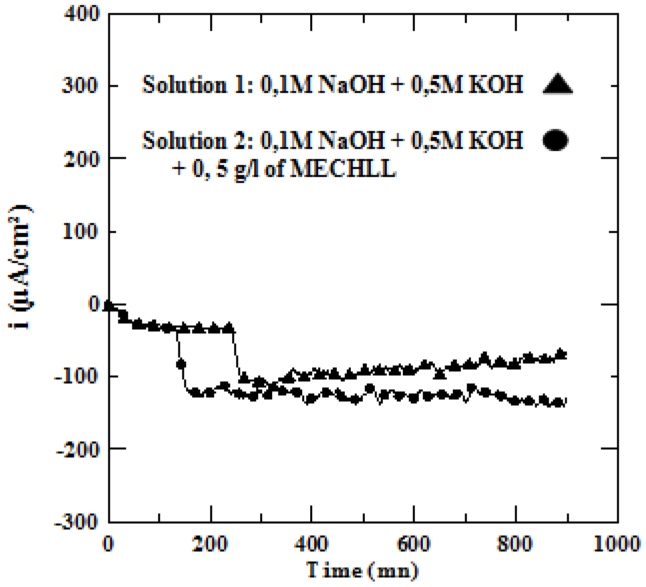


Figure 4. Evolution with time of currents for reinforcement steel in different solutions at initial fixed potential E = - 630 mV.

The evolution of current density at fixed potential (E = -630 mV) without and with inhibitor in solution is presented in figure 4.

The curves present two levels of currents densities approximately at - 25µA/cm² and at - 100 µA / cm². The first current density level can be attributed to dissolved oxygen reduction and metal oxidation which tends to form a protective film in both solutions. The second current density level is obtained earlier in the case with inhibitor extract (after 2 H 30 mn) than in the case without inhibitor extract (4 H).

This behavior can be explained by the action of the inhibitor to enhance the formation of more protective film on the metal surface. Thus, this study allows us to reaffirm the results obtained in open circuit potential and to say that extract inhibitor forms more protective layer on the surface of reinforcement steel.

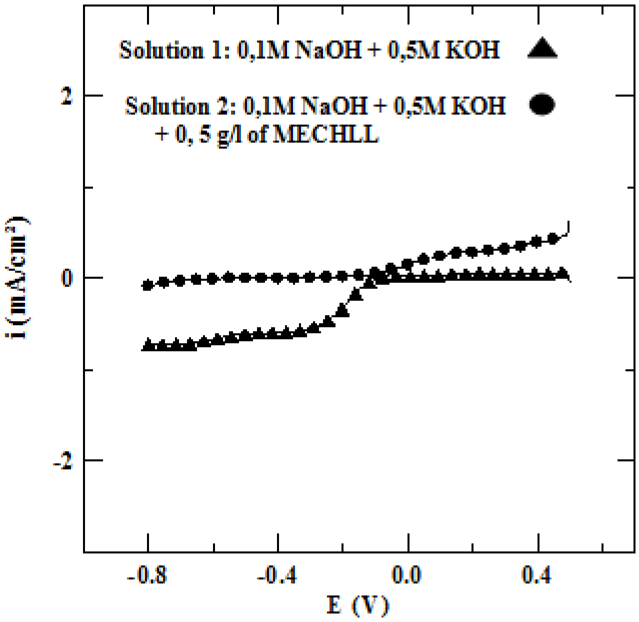


Figure 5. Linear polarization curve of platinum electrode.

On the other hand, the polarization curve of platinum electrode (figure 5) in the presence of inhibitor extract does not make up the activity behavior of the latter in the range of studied potential. Also, the presence of the inhibitor in the solution inhibits the reduction reaction of oxygen on platinum.

In the objective to have more information about the process which happened in the interface of the metal / electrolyte, some investigations have being made using electrochemical impedance spectroscopy study.

3.4 Electrochemical impedance spectroscopy (E.I.S) study.

The corrosion behavior of R.S, in alkaline solution in presence and absence of inhibitor is investigated by the electrochemical impedance spectroscopy (EIS) at 25°C at different immersion time.

The inhibition efficiency is calculated as follow:

$$E_{Rp}\% = [(R^{i}_{p}-R_{p}^{\circ})/R^{i}_{p}] \, x100 \qquad (1)$$

R^{i}_{p} and R_{p}° are respectively polarization resistances with and without Chamaerops Humilis L inhibitor.

The polarization resistance (R_p) values are deduced from impedance spectrum at low frequency limit.

3.4.1 Effect of Chamaerops humilis L. extract leaves

Figure 6, displays the Nyquist plots for R.S electrode immersed in 0,1 M NaOH + 0,5 M KOH without and with various concentrations of inhibitor, it can be seen that, after the addition of inhibitor, the diameters of the capacitive loops hanged with increasing concentration of inhibitor , indicating an improvement of protective performance of surface film formed on electrode surface , and the activity of R.S was effectively reduced [23-24].

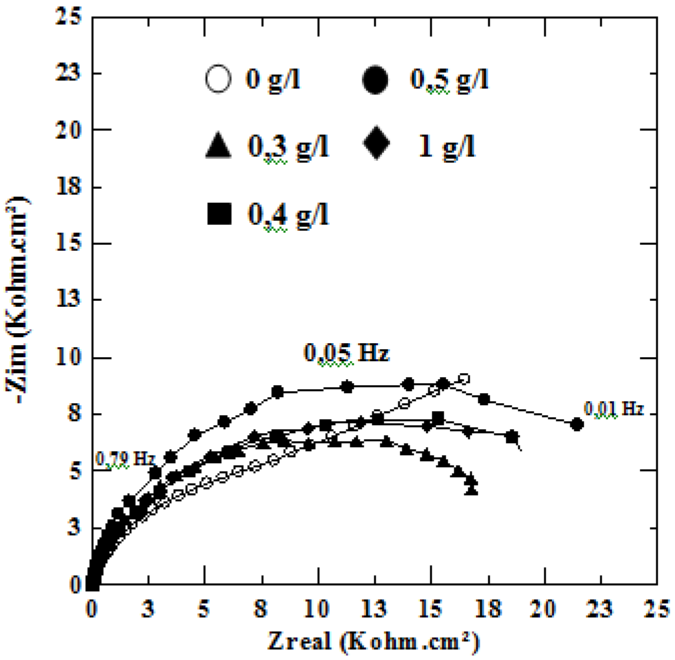


Figure 6. Nyquist plots for R.S electrode immersed in 0,1 M NaOH+ 0,5M KOH without and with extract of MECHLL.

From table 3, it can be seen that the values of R_p increased, whereas the values C_{ct} decreased with addition of various concentration of inhibitor, this suggests that the amount of inhibitor molecules adsorbed on the electrode surface.

The values of R_p indicates that the development of a protective film on electrode surface by the adsorption of inhibitor and reveals that the charge transfer reaction occurring in the protective film are restricted inhibitor introduction in solution. The results reflect that the surface structure of electrode is modified and its protection is significantly enhanced.

Table 3. Electrochemical impedance parameters for the corrosion of R.S in 0,1M NaOH+ 0,5M KOH without and with different concentration of MECHLL.

	Conc. (g/L)	R_p (Kohm.cm²)	C_{ct} (µF/cm²)	I.E %
Blank	0	11,04	57,63	---------
MECHLL extract	0,3	13,47	37,31	18%
	0,4	13,5	37,25	18,2%
	0,5	19,1	33,31	42%
	1	13,78	36,47	19,9%

3.4.2 Effect of time immersion with and without Chamaerops humilis L. extract leaves.

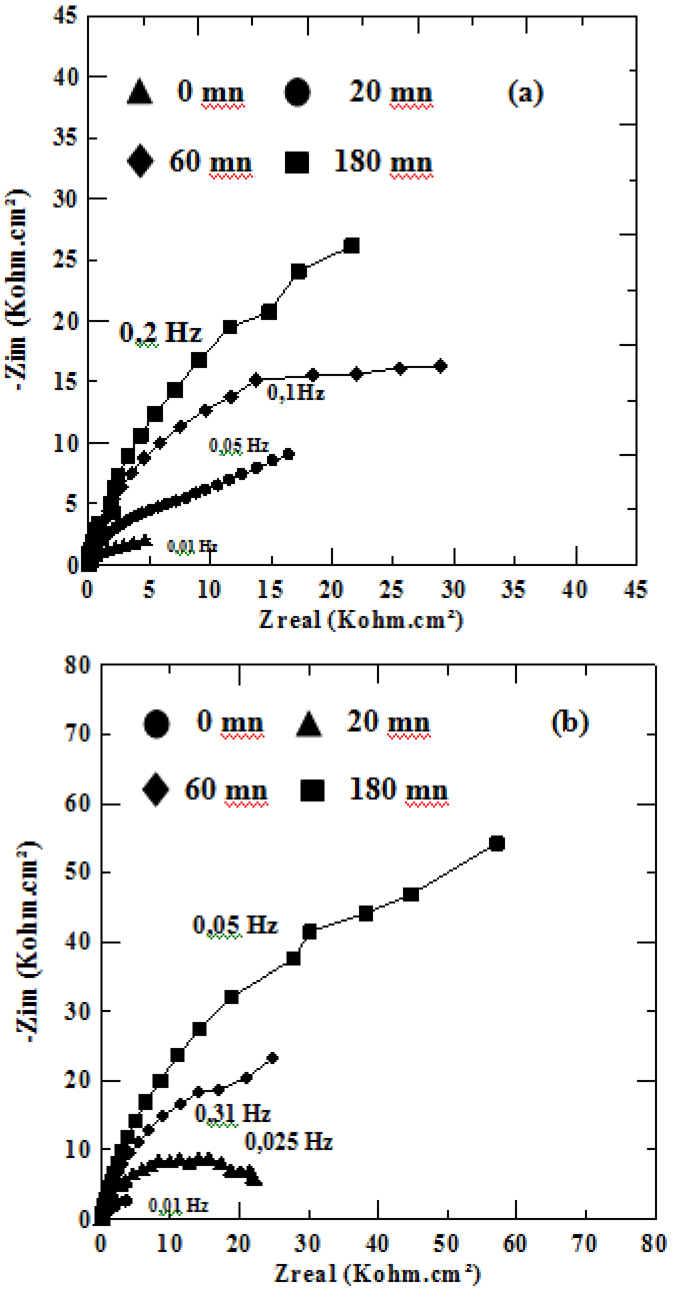


Figure 7. Nyquist plots without **a)** and with **b)** 0,5g/L of MECHLL for R.S electrode in 0,1 M NaOH+0,5M KOH at different immersion times.

The results obtained (Figure 7) show that the polarization resistance of the R.S without inhibitor increases according to immersion time. It can be explained by the development of the protective film. Thus the protective barrier passed from a porous and active surface to a compact and almost inactive surface.

The addition of the inhibitor is translated by a significant increase of the polarization resistance. Consequently decrease of associated capacitance with immersion time. Thus, the inhibitor plays an important role in the protection of the surface of the steel.

Table 4. Electrochemical impedance parameters for the corrosion of R.S in 0,1M NaOH+ 0,5M KOH without and with the MECHLL at different immersion times.

Immersion Time (mn)	Concentration of MECHLL (g/L)	R_p (Kohm.cm²)	C_{ct} (µF/cm²)	I.E %
t = 0 min	0	4,7	337,2	-------
	0,5	8,1	248	41,6%
t = 20 min	0	11	57,6	-------
	0,5	19	33,3	42,2%
t = 60 min	0	30,3	26,2	-------
	0,5	46,8	17	35,15%
t = 180 min	0	61,9	20,6	-------
	0,5	106,6	14,9	42%

According to table 4, we note that the inhibition efficiency is independent on immersion time because the values of this later are practically constant (figure 8).

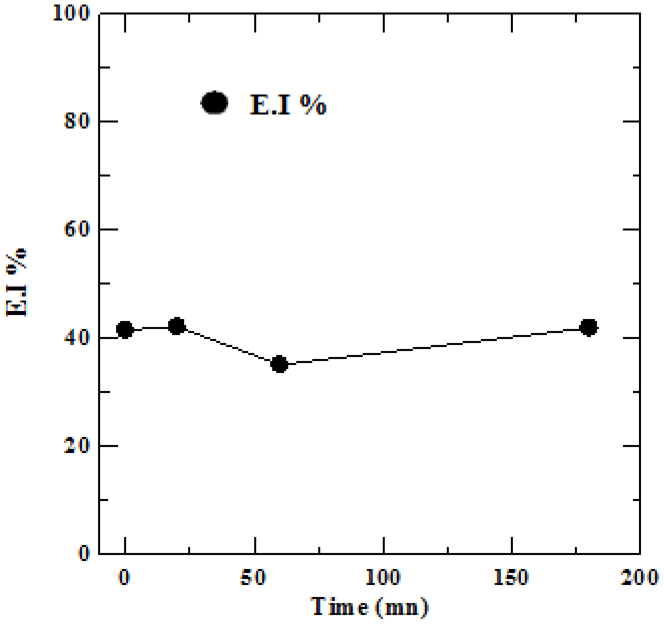


Figure 8. Evolution of inhibition efficiency with immersion time.

3.5. Adsorption isotherm.

Inhibition effects are based on the adsorption of molecules onto the metal surface to form an impermeable protective film and shielding it from the corrosive media. On the other hand, the adsorbed molecules can combine with the oxide layer on the metal (rust deposited) and react chemically to produce a more protective surface network by changing the film structure. The adsorption mechanism of organic compounds performs either directly, on the basis of donor-acceptor interactions between relatively loosely bound electrons such as in anions and organic molecules and/or the heterocyclic compound which has lone pair electrons or the π-electrons with the vacant d-orbitals of iron atoms of metal. Some parameters of organic molecule size, number of functional groups, polarity that contributed to the formation of the strongest bonding or rate of adsorptions of inhibitor compounds onto the surface could affect the adsorption mechanism or inhibition action [25].

The Langmuir adsorption isotherm provides a simple mechanistic picture of the adsorption process and gives rise to a relatively simple mathematical expression. The Langmuir adsorption isotherm may be written the following rearranged form:

$$C/\theta = 1/K + C \quad \text{or} \quad \theta/(1-\theta) = KC \qquad (2)$$

Where C is the concentration of inhibitor, K is the adsorptive equilibrium constant, θ is the surface coverage.

Taking into account that the evaluated capacity is proportional to the surface area not covered by the inhibitor, the fraction of the surface covered by adsorbed molecules was determined according to the ratio:

$$\theta = (C^{\circ}_{ct} - C^{i}_{ct} / C^{\circ}_{ct}) \qquad (3)$$

Where C°_{ct} is the charge – transfer capacity measured in the absence and C^{i}_{ct} in the presence, of the inhibitor [26].

The standard adsorption free energy (ΔG_{ads}) may be estimated using:

$$K = 1/C_{water} \exp(-\Delta G^{\circ}_{ads}/RT) \text{ or } \Delta G^{\circ}_{ads} = -RT \ln(C_{water} . K) \qquad (4)$$

Where C_{water} = 1000 expressed in g/L, R is the molar gas constant ans T is the temperature (25°C).

The standard adsorption free energy ΔG°_{ads}, which can characterize the interaction of adsorption between molecules and metal surface, was calculated. Generally, values of ΔG°_{ads} up to -20 $KJmol^{-1}$ are associated to physisorption type. The inhibition acted due to the electrostatic interactions between the charged molecules and the charge metal. The values of ΔG°_{ads} around -40 $KJmol^{-1}$ or smaller were associated with chemisorptions as a result of sharing or transfer of electrons from organic molecules to the metal surface to from a coordinate type of bond (chemisorptions) [27-28].

Figure 9 shows that the relationship between C_{inh}/θ and C_{inh}, The obtained curve is a straight line and all the slopes was very close to unity (2,6824). This behavior suggests that the adsorption of MECHLL on reinforcement steel surface followed the Langmuir adsorption isotherm with K= 1, 46 Lg^{-1}. The deduced value of standard free energy of adsorption ΔG°_{ads} is -18,05 KJ/mol.

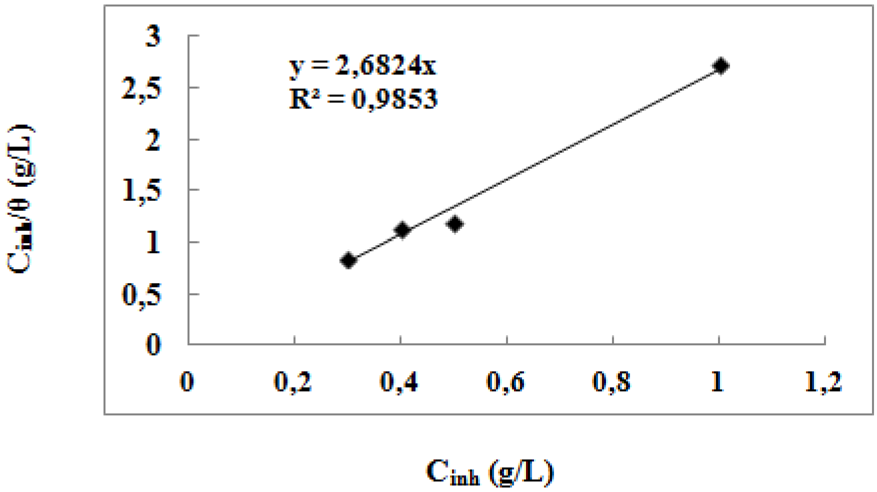


Figure 9. Langmuir adsorption plots for R.S electrode immersed in 0,1 M NaOH+0,5M KOH at different concentration of MECHLL..

The negative values of ΔG_{ads} indicate the stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process and also chemical and physical adsorption can occur together, but any adsorbed layers beyond the first must be physically adsorbed [27].

4. CONCLUSIONS

(i). The methanol extract of Chamaerops humilis L. leaves indicated the presence of 12 compounds, Lucenin 2 (42, 29%) is the major compound.

(ii). The inhibition efficiency increases with increase of inhibitor concentration to attain a maximum value of 42 % at 0, 5 g/l of chamaerops humilis L. leaves extract.

(iii). EIS plots of reinforcement steel showed that polarization resistance increases with increase of inhibitor concentration.

(iv). The inhibition efficiency is independent on immersion time.

(v). The action of methanol extract of Chamaerops humilis L. leaves obeys the Langmuir adsorption isotherm.

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