

The Palm oil from seed of *Phoenix dactylifera* (Oil of both Deglet Nour and Kentichi) as a natural antioxidants and Environment-Friendly inhibitors on the Corrosion of mild Steel in HCl 1M

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Abstract

The flora of Republic of Algeria comprises a lot of Palm species, including *Phoenix dactylifera*. In this work, we used the Palm oil from seed of *Phoenix dactylifera* (Oil of both Deglet Nour and Kentichi). The objective of this study is divided into two parts. Firstly, determine the antioxidant activity of Palm oil from seed of *Phoenix dactylifera* (Oil of both Deglet Nour and Kentichi) according to the DPPH radical scavenging assay to suggest it as a new potential source of natural antioxidants, secondly, study the effect of inhibiting Palm oil from seed of *Phoenix dactylifera* (Oil of both Deglet Nour and Kentichi) on corrosion of mild steel in hydrochloric acid by electrochemical methods. Furthermore, The DPPH scavenging activity of Oil of both Deglet Nour and Kentichi increased in the order, Deglet Nour Oil < Kentichi Oil < ascorbic acid. The results of the polarization curves show that the corrosion current density decreases 577.9 $\mu\text{A}/\text{cm}^2$ to 58 $\mu\text{A}/\text{cm}^2$ and to 59.3 $\mu\text{A}/\text{cm}^2$ after addition of the inhibitor (oil of Deglet Nour and Kentichi respectively). The charge transfer resistance increases 21.69 ohm.cm^2 to 186.5 ohm.cm^2 and to 222.8 ohm.cm^2 in the electrochemical impedance spectrum after addition of oil of Deglet Nour and Kentichi respectively. The inhibition of the compound effect is attributed to the formation of a film on the surface of the steel.

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I. Introduction

Plants extracts and natural products became nowadays very searched target for the discovery of safe and effective antioxidant and free radical scavenging activity agents [1,2]. Due to their beneficial effects and low toxicity, they are proposed by scientist for the replacement of synthetic antioxidant such as butyl-hydroxyl-toluene (BHT) and butyl-hydroxy-anisole (BHA) which are suspected to be carcinogenic [3,4]. The antioxidant activity of a compound is its ability to resist oxidation, that is to say, the ability to scavenge free radicals such as hydroxyl radicals ($\text{OH} \bullet$) and superoxide ($\text{O}_2 \bullet$). The best known antioxidants are the β -carotene (provitamin A), ascorbic acid (vitamin C), tocopherol (vitamin E) as well as phenolic compounds [5-6]. Beside the antioxidant and free radical scavenging activity, plants extracts became also a target for the discovery of natural inhibitors of steel corrosion. The use of inhibitors is one of the best methods of protection against corrosion of metals [7, 8]. Most corrosion inhibitors are organic compounds having hetero atoms in their longest carbon chain or aromatic [7-9]. The effectiveness of these compounds as corrosion inhibitors can be attributed to the number of pairs of mobile electrons [10]. However, there is a growing concern about the toxicity of most corrosion inhibitors. The toxic effect not only affects the lives organizations, but also poisons the environment [7, 8]. Due to the toxicity of certain corrosion inhibitors, recently, several studies have been carried out on the inhibition of corrosion of metals by plant extract. In this context, our laboratory adopted a strategy of evaluation of these molecules against corrosion of mild steel in acid media [11-21], they have been found to be very efficient corrosion inhibitors for mild steel in acid media. In this paper, we study the antioxidative properties using DPPH method and the inhibitive action of the Palm oil from seed of *Phoenix dactylifera* (Oil of both Deglet Nour and Kentichi), on corrosion behaviour of mild steel in 1M HCl by gravimetric method and electrochemical techniques such as potentiodynamic polarisation, linear polarisation and electrochemical impedance spectroscopy (EIS).

II. Experimental

II.1. Plant material

The date Deglet Nour and Kentichi were collected in the region of Tolga (Algeria) on May 2012. The seeds were separated from the fruits, dried and crushed separately milled in a heavy-duty grinder to pass 1-2 mm screens and then preserved at -20°C .

II.2. Extraction and procedure

Powder date seeds (255g) were subjected to oil extraction, with petroleum ether using Soxhlet apparatus. The extraction process continued for 4-6 h. The solvent was evaporated on rotary evaporator under reduced pressure and the produced oil was collected, weighed, stored in a dark container in a deep-freeze (4°C) till subsequent analyses.

II.3. Characterization and chemical composition of oil

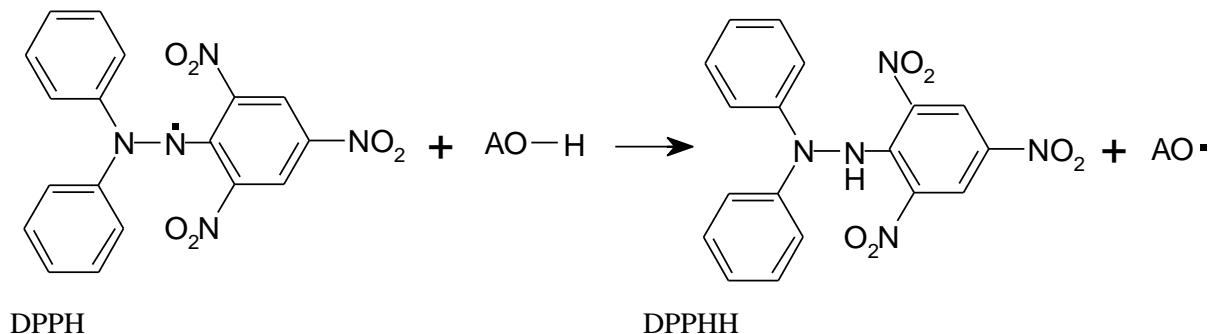
GC/MS: The oil was analyzed on a Shimadzu gas chromatograph Model GC2010 coupled to a Shimadzu MS model QP2010, equipped with a DB5 MS column (30m x 0.25mm; $0.25\mu\text{m}$), programming from 50°C (5 min) to 300°C at $5^\circ\text{C}/\text{mn}$, 5 min hold. Helium was used as carrier gas (1.0 ml/min); injection in split mode (1:30); injector and detector temperature, 250°C and 280°C respectively. The MS working in electron impact mode at 70 eV; electron multiplier, 2500 V; ion source temperature, 180°C ; mass spectra data were acquired in the scan mode in m/z range.

II.3.1. Identification of components

The oil components were identified based on their retention indices (determined with reference to a homologous series of normal alkanes), and by comparison of their mass spectral fragmentation patterns with those reported in the literature [22, 23] and for the major components.

II.4. Antioxidant activity

The free radical-scavenging activities of solvent extracts were measured using 1,1-diphenyl-2-picrylhydrazyl (DPPH) as described by Hatano et al. [24], antioxidants react with the stable free radical DPPH (deep violet color) and convert it to 1,1-diphenyl-2-picrylhydrazine with discoloration.



Where: (AO-H) represents a compound capable of yielding hydrogen to DPPH radical (violet) to transform it into picryl diphenyl hydrazine (yellow) [25]. Various different concentrations prepared in ethanol for the different samples and standard studied are between 0.2 to 2 µg / ml were added to 3.9 ml of a DPPH radical solution in ethanol. The mixture was strongly shaken and left to stand at room temperature for 30 min in the dark. The absorbance was measured at 517 nm against a blank. The radical-scavenging activity was expressed as percentage of inhibition (I%) according to the following formula [26]:

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

Where A control is the absorbance of the control reaction and A sample is the absorbance of the test compound. The sample concentration providing 50% inhibition (IC₅₀) was calculated from the graph of inhibition percentage against sample concentration. Tests were carried out in triplicate. Ascorbic acid was used as a positive control.

II.5. Solutions and mild steel samples preparation

The electrolyte is a solution of HCl 1 mol / L, prepared using double distilled water. All chemicals were of analytical grade reagents. The experiments were performed in non-agitated conditions and naturally ventilated conditions. The concentration range of oil employed varies from 0.5 to 4 mL/L and from 0.5 to 5 mL/L for Deglet Nour oil and Kentichi oil respectively. 100 ml of electrolyte was used for each experiment. The working electrode is prepared from the steel samples with a composition (in% by weight)(0.21% C, 0.38% Si, 0.09% P, 0.01% Al, 0.05% Mn, 0.05% S), an area of 1 cm² was used as electrodes working for polarization measurements and EIS. The exposed area was mechanically abraded with 400, 500 and 600 sandpaper, washed with double distilled water, degreased with acetone and finally dried before each experiment. Electrochemical measurements were carried out in a conventional three electrode cylindrical glass cell. The working electrode (WE), in the form of a disc cut from steel, has a geometric area of 1 cm². A saturated calomel electrode (SCE) and a platinum electrode were used as reference and auxiliary electrodes, respectively.

II.6. Weight loss measurements

The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. Although these tests are simple, there is no simple way to extrapolate the results to predict the lifetime of the system under investigation. Moreover, some corrosion processes occur with no significant mass change (e.g. pitting corrosion) making them difficult to detect by gravimetric method [27-29]. The simplest way of measuring the corrosion rate of a metal is to expose the sample to the test medium (e.g. sea water) and measure the loss of weight of the material as a function of time. The gravimetric test is based on the immersion of the steel plates in iron, in 100 ml of a 1M HCl solution containing the inhibitor (Deglet Nour oil & Kentichi oil) at different concentrations, after be degreased, polished and weighed. Immersion is subjected to a temperature of 308 ° K to 6 hours. Temperature corrosive environment is a factor that can affect the efficacy of inhibiting it. Given the importance of this factor, we performed tests of mass loss of steel in 1 M HCl with and without addition of the inhibitors at different temperatures between 313 and 343 ° K.

II.7. Electrochemical measurements

As mentioned in the previous application notes, most corrosion phenomena are of electrochemical nature and consist of reactions on the surface of the corroding metal. Therefore electrochemical tests methods can be used to characterise corrosion mechanisms and predict corrosion rates.

II.7.1. Potentiodynamic polarization

The polarization curves were recorded using a potentiostat type PGZ Volta Lab 100 to a scan rate of 1 mV/Sec. The electrode of steel was maintained at the corrosion potential for 30 minutes and the following pre-polarized -800 to -200 mV/SCE for 10 min, all experiments were repeated three times at the desired temperature of ± 1 °C. The potential was swept in the anodic potential. All test solutions were deaerated in the cell using pure nitrogen for 30 min before the experiment. During each experiment, the test solution was mixed with a magnetic stirrer and gas bubbler was maintained. Corrosion current densities were obtained from the polarization curves by linear extrapolation of the Tafel curves. Prior to the electrochemical measurement, a stabilization period of 30 minutes was allowed, which was proved to be sufficient to attain a stable value of corrosion potential (E_{corr}). Tafel polarization curves were plotted at a polarization scan rate of 1 mV/s. Anodic and cathodic curve slopes were extrapolated to corrosion potential, for the determination of the corrosion current densities (I_{corr}). The Tafel equations predict a straight line for the variation of the logarithm of current density with potential. Therefore, currents are often shown in semi logarithmic plots known as Tafel plots. This type of analysis is referred to as Tafel Slope Analysis. The Tafel slope analysis tool provides a quick estimation of the corrosion rate and the polarization resistance. The corrosion rate is calculated from the estimated corrosion current, I_{corr} , obtained from the intercept of the two linear segment of the Tafel slope.

II.7.2. Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy (EIS) has many advantages in comparison with their electrochemical techniques. During EIS experiments, a small amplitude ac signal is applied to the system being studied. Therefore, it is a non-destructive method for the evaluation of an idea range of materials, including coatings, anodized films and corrosion inhibitors. It can also provide detailed information of the systems under examination; parameters such as corrosion rate, electrochemical mechanisms and reaction kinetics, detection of localized corrosion, can all be determined from these data. Electrochemical impedance spectroscopy (EIS) was carried out with the same equipment

used for the polarization measurements, leaving the frequency response analyzer out of consideration. Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mV/s. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz was superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potential after 30 min of exposure. All potentials were reported versus saturated calomel electrode (SCE). The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility. All electrochemical studies were carried out with immersion time of 1 hour, with different inhibitory concentrations of Deglet Nour oil & Kentichi oil, at 308 °K.

III. Resultants and discussion

III.1. Fatty acid composition

From the GC-MS analysis, it appears that the two varieties of the palm oil (Deglet Nour & Kentichi) are characterized by many fatty acids.

Table 1. Fatty acid compositions of the seeds of Deglet Nour oil (%).

Fatty acid	R _I	%
Lauric acid, methyl ester	9.125	25.43
Myristic acid, methyl ester	11.556	12.35
Palmitic acid, methyl ester	13.784	10.27
9-Octadecenoic acid, methyl ester	15.762	35.40
8,11-Octadecadienoic acid, methyl ester	15.836	16.55

Table 2. Fatty acid compositions of the seeds of Kentichi oil (%).

Fatty acid	R _I	%
Myristicin	10.598	32.01
Apiole	12.573	26.33
Palmitic acid, methyl ester	13.783	7.63
Linoleic acid, methyl ester	15.838	6.96
Bicyclo [6.4.0]dodeca-1(8),4-diene-10,11-dicarboxylic acid	16.251	5.49
Eremanthin	16.400	21.58

R_I: Retention Indices

III.2. Antioxidant activity

Results of free radical scavenging activity of Deglet Nour Oil, Kentichi Oil and Ascorbic Acid (positive control) are given in Table 3. Data in the table indicated that the DPPH scavenging activities (%) were increased significantly with increasing the concentration of the studied samples from 10 to 80 µL/mL.

Table 3. The antioxidant activity of Deglet Nour Oil, Kentichi Oil and Ascorbic Acid (positive control) at different concentrations.

Samples	Antioxidant Activity					
	Concentrations de l'extrait ($\mu\text{L/mL}$)	10	20	40	60	80
Deglet Nour Oil	Scavenging effect on DPPH (%)	27.15	30.71	46.44	60.65	61.92
	DPPH IC_{50} ($\mu\text{L/mL}$)	50.53				
	Concentrations de l'extrait ($\mu\text{L/mL}$)	10	20	40	60	80
Kentichi Oil	Scavenging effect on DPPH (%)	30.71	35.02	44.16	57.86	64.21
	DPPH IC_{50} ($\mu\text{L/mL}$)	49.22				
	Concentrations ($\mu\text{g/mL}$)	10	20	40	60	80
Ascorbic Acid	Scavenging effect on DPPH (%)	42.89	54.31	85.02	90.1	92.89
	DPPH IC_{50} ($\mu\text{L/mL}$)	10.7				

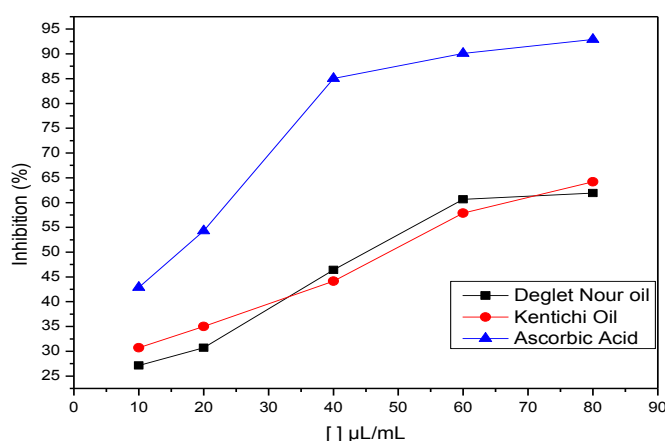


Figure 1. Antioxidant power of Deglet Nour Oil, Kentichi Oil and Ascorbic Acid, OD reading after 30 min of incubation.

Inspection of Table 3, the antioxidant activity of Kentichi Oil is greater than Deglet Nour Oil. This activity increases with the concentration, this is explained by the fact that the studied samples give hydrogen to DPPH who then converted to the color violet in yellow and absorbs less light [30]. When the concentration is high, more antioxidants, DPPH is reduced, so less it absorbs light passing through it. Generally, *Palm Oil seeds* shows a good antioxidant activity at the concentration of 80 $\mu\text{L} / \text{mL}$ reach until 61.92 % and 64.21 % for Deglet Nour Oil and Kentichi Oil respectively (Figure 1). Both Oil of Deglet Nour and Kentichi exhibit a lower activity than that of ascorbic acid (92.89 %). The Kentichi Oil had the highest radical scavenging activity with the lowest IC_{50} value (49.22 $\mu\text{L/mL}$). This value was higher with Deglet Nour Oil (IC_{50} is 50.53 $\mu\text{L/mL}$). Additionally the Kentichi Oil has a lower scavenging capacity than Ascorbic Acid (IC_{50} is 10.7 $\mu\text{L/mL}$).

III.3. Electrochemical impedance measurements

Among the different electrochemical techniques that can be used to study corrosion inhibitors, EIS appears as powerful tool for the information that can provide, as for example, double layer capacitance, C_{dl} , and polarization resistance, R_p , values. Changes in these parameters as a function of time or with respect to other variables, allow

obtaining important information about the kinetics of the corrosion process being involved [31-32]. The impedance measurements were carried out using AC signals of amplitude 10 mV peak to peak, the open circuit potential using Tacussel Radiometer PGZ 100 Frequency Response Analyzer in a frequency range of 100 kHz to 10 mHz. The inhibition Efficiency E (%) was estimated from the charge transfer resistance measured, R_{ct} , Values using the equation (1):

$$E\% = ((R_{ct} - R_{ct}^0) / R_{ct}) \times 100 \quad (1)$$

Where R_{ct}^0 and R_{ct} are the charge-transfer resistance values in the absence and presence of the inhibitor, respectively. All electrochemical measurements were done in unstirred and non de aerated solutions. The electrochemical impedance plots for mild steel in 1M HCl solution in the absence and presence of various concentrations of oil of Deglet Nour and oil of Kentichi are shown in Figure 2 & 3. Table 4 summarizes impedance data from the EIS experiments carried out in the absence and presence of increasing the inhibitors concentrations.

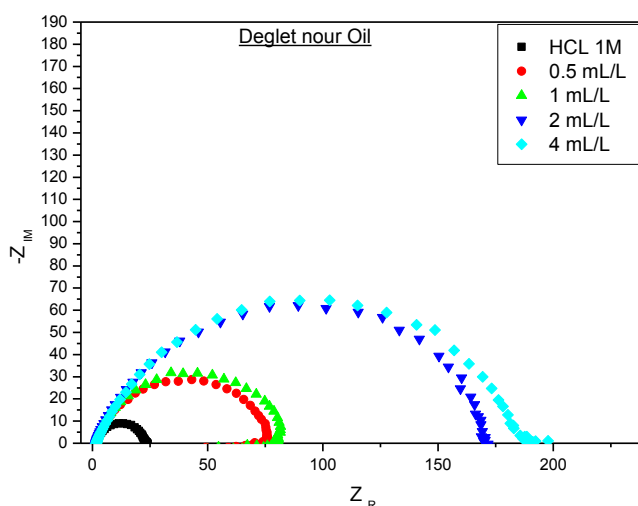


Figure 2. Nyquist plots in absence and presence of different concentrations of Deglet Nour oil in HCL 1M.

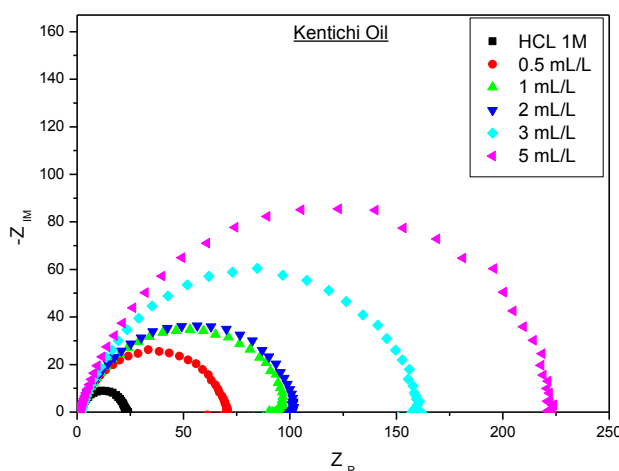


Figure 3. Nyquist plots in absence and presence of different concentrations of Kentichi oil in HCL 1M.

The corrosion behaviour of steel, in acidic solution in the absence and presence of Deglet Nour oil and Kentichi oil, is also investigated by EIS method at E_{corr} and 308 °K after 30min of immersion (Fig. 2, 3). The charge-transfer

resistance (R_{ct}) values are calculated from the difference in impedance at lower and higher frequencies. The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (2)$$

Table 4. Corrosion parameters obtained by impedance measurements for mild steel in HCL 1M at various concentrations of Deglet Nour and Kentichi oil.

Inhibitors	concentration	R_{ct} (ohm.cm ²)	f_{max} (Hz)	C_{dl} (μF/cm ²)	E (%)
Deglet Nour oil	HCL 1M	21.69	100	73.37	-
	0.5 mL/L	76.68	40	51.88	71.71
	1 mL/L	83.14	40	47.86	73.91
	2 mL/L	174.5	20	45.6	87.53
	4 mL/L	186.5	20	42.66	88.37
Kentichi oil	0.5 mL/L	69.23	50	45.98	68.67
	1 mL/L	99.77	40	39.88	78.26
	2 mL/L	102.5	40	38.81	78.84
	3 mL/L	159.5	25	39.91	86.4
	5 mL/L	222.8	10	35.72	90.26

The impedance parameters derived from these investigations are mentioned in Table 4. It is worth noting that, the presence of inhibitor does not alter the profile of impedance diagrams which are almost semi-circular (Fig. 2, 3), indicating a charge transfer process mainly controls the corrosion of steel. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon is interpreted by the in homogeneity of the electrode surface arising from surface roughness or interfacial phenomena [33, 34]. In fact, the presence of Deglet Nour oil and Kentichi oil enhances the value of R_{ct} in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in the values of C_{dl} means that the adsorption of this oil takes place on the metal surface in acidic solution. We also note the increase of the value of R_{ct} with the inhibitor concentration leading to an increase in the corrosion inhibition efficiency. The best result for the inhibition efficiency of Deglet Nour oil was obtained at a concentration of 4 mL/L, with efficiency equal to 88.37 % and 90.26 % for Kentichi oil at a concentration of 5 mL/L.

III.4. Tafel polarization curves

The type of experiment was performed. Immediately upon immersion of the samples in the electrolytes, the open circuit potential (OCP) was monitored for one hours. This was followed by potentiodynamic anodic polarisation measurements. Lastly, in order to investigate whether corrosion products formed on the sample surfaces, the anodic polarisation tests were carried out on the same surface and in the same test solution. All tests were done at room temperature using electrolytes that were not de-aerated during testing. Polarization curves for mild steel in presence and absence of different concentrations of Deglet Nour oil and Kentichi oil in non aerated solutions are shown in Figure 4, 5. The extrapolation of Tafel straight line allowed the calculation of the corrosion current density (I_{corr}). The values of I_{corr} , the corrosion potential (E_{corr}), cathodic Tafel slope (β_c), and inhibition efficiency (E %) are

given in Table 5 for inhibitors oil. In this case, the efficiency of corrosion inhibition (% E) was determined according to equation (3) :

$$E(\%) = \frac{I^{\circ}_{corr} - I_{corr}}{I^{\circ}_{corr}} \times 100 \quad (3)$$

Where I°_{corr} and I_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential.

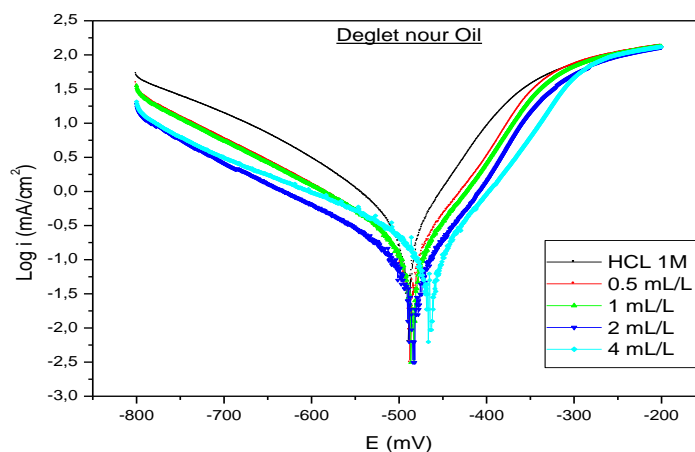


Figure 4. Tafel polarization curves in HCL 1M with and without Deglet Nour oil at different concentrations.

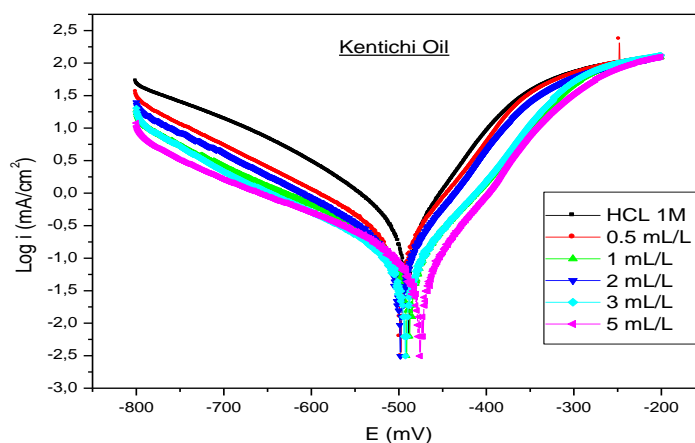


Figure 5. Tafel polarization curves in HCL 1M with and without Kentichi oil at different concentrations.

Inspection of these results reveals that in presence of inhibitors, the value of corrosion density (I_{corr}) was decreased. This behaviour reflects its ability to inhibit the corrosion of mild steel in 1M HCl solution. Both the anodic and cathodic current densities were decreased in figure 4 and 5, indicating that Deglet Nour oil and Kentichi oil suppressed both the anodic and cathodic reactions through adsorption on the mild steel surface. This suggests that Deglet Nour oil and Kentichi oil act as mixed type corrosion inhibitor for mild steel in 1M HCl solution. Generally, the modes of the inhibition effect of inhibitors are classified into three categories [35, 36]: geometric blocking effect of adsorbed inhibitive species, active sites blocking effect by adsorbed inhibitive species, and electro catalytic effect of the inhibitor or its reaction products. It has been discussed in the case of the first mode that inhibition effect comes from the reduction of the reaction area on the surface of the corroding metal, whereas for the other two modes the inhibition effects are due to the changes in the average activation energy barriers of the anodic and cathodic reactions of the

corrosion process. The cathodic Tafel slope (β_c) show slight changes with the addition of inhibitors, which suggests that the inhibiting action occurred by simple blocking of the available cathodic sites on the metal surface, which lead to a decrease in the exposed area necessary for hydrogen evolution and lowered the dissolution rate with increasing Palm oil concentration (table 5). The parallel cathodic Tafel plots obtained in Figure 4 and 5 indicate that the hydrogen evolution is activation controlled and the reduction mechanism is not affected by the presence of inhibitors [37, 38].

Table 5. Electrochemical parameters of mild steel at various concentrations of Deglet Nour oil and Kentichi oil in HCL 1M.

Inhibitors	Concentration	$-E_{\text{Corr}}$ (V)	β_c (mV/dec)	I_{Corr} ($\mu\text{A}/\text{cm}^2$)	E (%)
	HCL 1M	0.49	-147.7	0.5779	-
	0.5 mL/L	0.48	-149	0.2317	59.9
Deglet Nour oil	1 mL/L	0.48	-150.7	0.2144	62.9
	2 mL/L	0.48	-154	0.1083	81.26
	4 mL/L	0.46	-126.3	0.058	89.26
	0.5 mL/L	0.49	-145.4	0.2203	61.88
	1 mL/L	0.49	-180	0.1627	71.85
Kentichi oil	2 mL/L	0.49	-142.7	0.1548	73.21
	3 mL/L	0.49	-149.6	0.0869	84.96
	5 mL/L	0.47	-112.4	0.0593	89.74

III.5. Effect of temperature

The effect of temperature on the corrosion behaviour of steel in 1 M HCl containing inhibitor at optimum concentration is studied in the temperature range 313–343 K using weight loss measurements at 6 h. The data of corrosion rates and corresponding efficiency collected are presented in Table 6 & Fig 6, shows clearly that inhibitors retards the corrosion rate of the mild steel in the test solutions.

Examination of Table 6 revealed that the corrosion rate increases both in the uninhibited and in the inhibited acid solution with the rise of temperature. The presence of inhibitor leads to decrease of the corrosion rate. E% depends upon the temperature and increases with temperature. The increase in E% indicates that the inhibitory effect of inhibitors is reinforced

at elevated temperature. In acidic solution, the corrosion rate is related to temperature by Arrhenius equation (4) and transition state equation (5) was used [39]:

$$CR = A \exp\left(\frac{-E_a}{R \times T}\right) \quad (4)$$

$$CR = \frac{R \times T}{N \times h} \exp\left(\frac{-\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{R \times T}\right) \quad (5)$$

where CR is the corrosion rate, R the gas constant, T the absolute temperature, A the pre-exponential factor, h the Plank's constant and N is Avogadro's number, E_a the activation energy for corrosion process, ΔH_a the enthalpy of activation and ΔS_a the entropy of activation. The apparent activation energy (E_a) at optimum concentration of Deglet Nour oil and Kentichi oil was determined by linear regression between $\ln(C_R)$ and $1/T$ (Fig. 7) and the result is shown in Table 7.

Table 6. Corrosion parameters for mild steel in HCL 1M in absence and presence of optimum concentration of the inhibitors studied (Deglet Nour oil & Kentichi oil) at different temperatures.

Temperature (°K)	Inhibitors	CR(mg/cm ² .h)	E (%)
313	HCL 1M	1.2996	-
	Deglet Nour oil	0.2469	81
	Kentichi oil	0.2704	79.19
323	HCL 1M	1.828	-
	Deglet Nour oil	0.4065	77.76
	Kentichi oil	0.636	65.21
333	HCL 1M	3.635	-
	Deglet Nour oil	0.9371	74.22
	Kentichi oil	1.4847	59.08
343	HCL 1M	6.3363	-
	Deglet Nour oil	1.8876	70.21
	Kentichi oil	2.9571	53.33

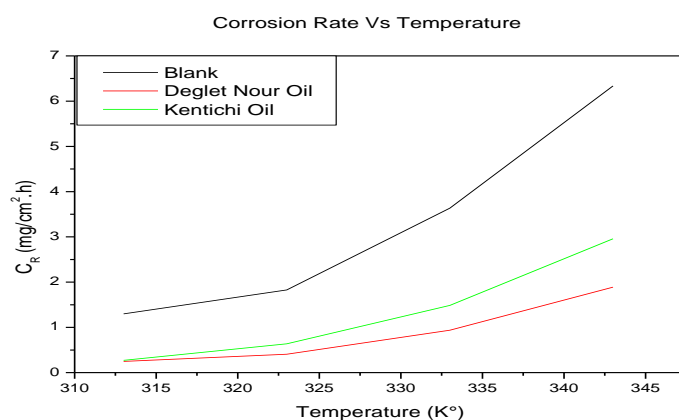


Figure 6. Variation of CR in 1M HCl on steel surface without and with of optimum concentration of Deglet Nour and Kentichi oils at different temperatures.

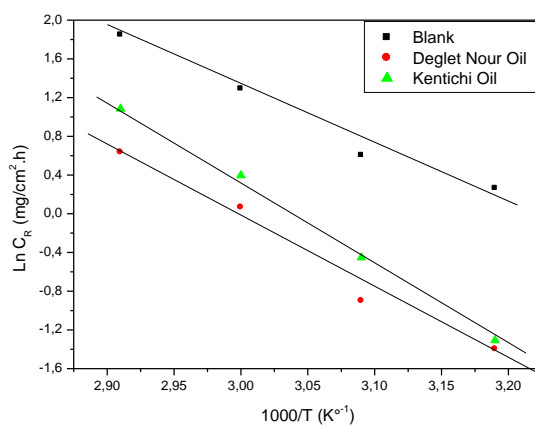


Figure 7. Arrhenius plots of ln CR vs. 1/T for mild steel in 1M HCl in the absence and the presence of Deglet Nour oil and Kentichi oil respectively at optimum concentration (4 mL/L , 5 mL/L).

Table 7. Activation parameters E_a , ΔH_a and ΔS_a for the mild steel dissolution in 1M HCl in the absence and the presence of Deglet Nour oil and Kentichi oil respectively at optimum concentration (4 mL/L, 5 mL/L).

Inhibitors	E_a (KJ/mol)	ΔH_a (KJ/mol)	ΔS_a (J/mol.K)
1M HCL	20.97	45.58	-98.3
Deglet Nour oil	63.02	59.08	-69.13
Kentichi oil	71.74	68.99	-35.93

Inspection of Table 7 showed that the value of E_a determined in 1M HCl containing Deglet Nour oil and Kentichi oil are higher (63.02 and 71.74 KJ/mol) than that for uninhibited solution (20.97 KJ/mol). The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage. The increase in activation energy could be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with increase in temperature. As adsorption decreases more desorption of inhibitor occur because these two opposite processes are in equilibrium. Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of steel comes in contact with aggressive environment, resulting increased corrosion rates with increase in temperature.

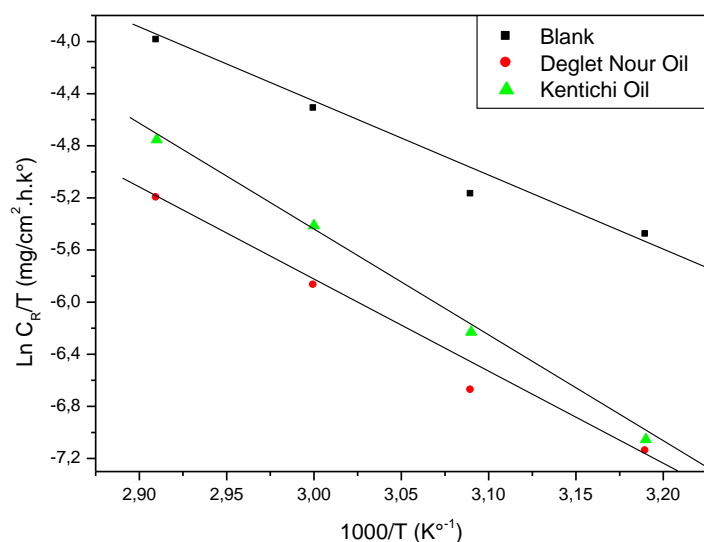


Figure 8. Arrhenius plots of $\ln C_R/T$ vs. $1/T$ for steel in 1M HCl in the absence and the presence of extract of Deglet Nour oil and Kentichi oil respectively at optimum concentration (4 mL/L, 5 mL/L).

Fig.8, showed a plot of $\ln C_R/T$ versus $1/T$. The straight lines are obtained with a slope ($\Delta H_a/R$) and an intercept of ($\ln R/Nh + \Delta S_a /R$) from which the values of ΔH_a and ΔS_a are calculated for Deglet Nour oil and Kentichi oil of analyzed and are given in Table 7. Inspection of these data revealed that the thermodynamic parameter (ΔH_a) for dissolution reaction of steel in 1M HCl in the presence of inhibitors are higher (59.08 and 68.99 kJ/mol) than that of in the absence of inhibitors (45.58 kJ/mol). The positive sign of ΔH_a reflect the endothermic nature of the steel dissolution process suggesting that the dissolution of steel is slow in the presence of inhibitors. Negative value of entropy (ΔS_a) imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactant to the activated complex.

IV. Conclusions

Finally, we can deduce that:

- The Palm oil seed (Oil of both Deglet Nour & Kentichi) can reduce the radical 2,2-diphenyl-1-picrylhydrazyl, so they have an antioxidant effect in vitro, and can be proposed as new potential sources of natural additives in the food and pharmaceutical industries.
- Tafel polarization measurements indicate that the two varieties of Palm oil act essentially as a mixed type inhibitors.
- The increase in the charge transfer resistance and decrease in double layer capacitance values, with the increase in the inhibitor concentration, showed that the two varieties of Palm oil formed protective layers on the mild steel surface, covering areas where HCl solution degrades and corrodes rapidly.
- Inhibition efficiency increases with increase in the concentration of Deglet Nour oil and Kentichi oil but decreases with rise in temperature.
- The corrosion process was inhibited by adsorption of the organic matter on the mild steel surface, obtaining the formation of the film on the metal/acid solution interface, decreasing the degradation of the material.
- Results obtained through weight loss measurements and electrochemical tests demonstrated that the two varieties of Palm oil act as efficient corrosion inhibitors of the mild steel in 1 M HCl solution.

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