The use of essential oil and extract of *Tetraclinis articulata* as eco-friendly corrosion inhibitors of carbon steel in hydrochloric acid solution

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ABSTRACT

The inhibiting action of Tetraclinis Articulata inhibitors was investigated as the corrosion inhibitors of mild steel in 1M HCl solution using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) methods, and weight loss measurements. The results revealed that both inhibitors of Tetraclinis Articulata were effective inhibitors, and the inhibition efficiencies obtained from polarization and weight loss experiments were in good agreement. The data obtained indicates that TCE and TCO behave as a mixed-type adsorbing onto the carbon steel surface according to the Langmuir isotherm inhibitors. Thermodynamic parameters such as activation energy and free energy of adsorption were calculated.

Keywords: Tetraclinis Articulata, adsorption, corrosion, inhibition, carbon steel, essential oil, extract, hydrochloric acid.
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INTRODUCTION

Corrosion is a process of major importance playing an interesting role in the economy and security, especially for the deterioration of metals and alloys [1]. Steel, an iron alloy has found wide applications in broad spectrum of industries and machines. It is also used as a construction material owing to its excellent mechanical properties and profitability; despite its tendency to corrosion [2]. Hydrochloric and sulphuric acids are the most practical solutions used for the industrial acid cleaning, oil well acidification, petrochemical processes and acid pickling which generally leads to serious metallic corrosion [3]. In order to reduce the corrosion rate of metals, the use of inhibitors is considered as one of the most practical methods for the protection against corrosion, especially in acid medium, where it is essential to prevent the dissolution of the metal and the acid consumption [4].

The most well-known organic compounds containing oxygen, sulphur and nitrogen which are used to reduce corrosion attack on steel, have been experimentally investigated [5-9]. Adsorption of these compounds on the metal surface blocks the active sites on the surface and thereby reduces the corrosion process [10-12]. The known hazardous effects of the most synthetic organic inhibitors and restrictive environmental regulations have made researchers to focalize their works to use natural products named green inhibitor and eco-friendly, as corrosion inhibitors [1, 3, 13-15]. Up till now, many green inhibitors have been used as effective corrosion inhibitors for iron or steel in acidic media, such as: plant extract [16, 17], especially essential oils [18, 19], or purified compounds [20, 21]. We have previously reported that pennyroyal oil [22], Argan oil [1], Fennel oil [13], jojoba oil [23], rosemary oil [24-26], Thymus oil [27, 28], Artemisia oil [29-31], lavender oil [32]. Menthol derivatives [33], allylpulegols [34], Eugenol and Acetyleugenol [35], Pulegone [36] and Limonene [37] have been found as naturally successful

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occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. Thuya Barbary known as Tetraclinis Articulata is endimic in the western Mediterranean region and it is also popular in the Moroccan traditional medicine. It is mainly used against intestinal and respiratory infections, diabetes and hypertension [38]. The aim of this paper is to evaluate the inhibitive action of Tetraclinis Articulata oil (TCO) and its extract (TCE) on corrosion behavior of carbon steel in 1M HCl using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The adsorption and inhibition efficiency of these inhibitors were investigated and the thermodynamic parameters in both the absence and the presence of these inhibitors were calculated.

MATERIALS AND METHODS

0.1. Solutions preparation

The acid solutions (1M HCl) were prepared by dilution of a Merck analytical reagent grade 37 % HCl and density 1.19 g/cm^3 (20°C) with double-distilled water. An assay by sodium hydroxide solution (1M NaOH) for monitoring normality is systematically carried out at each of the corrosive solution preparation. A Sample of the ground leaves of the Tetraclinis Articulata was collected from the area of Al Hoceima National Park (Morocco) in March. The dried plant material was stored in the laboratory at room temperature (298 K) and in the shade before the extraction.

- **Hydrodistillation apparatus and procedure**

The extraction of essential oil from the aerial parts of Tetraclinis Articulata was conducted by hydrodistillation using a Clevenger-type apparatus according to the method recommended in the European Pharmacopoeia [39]. The color of the Tetraclinis Articulata oil was yellow and the yield of hydrodistillation was 2.3% (v/w) according to the dry material. The essential oil obtained was dried under anhydrous sodium sulfate and stored in sealed glass vials at 4-5 °C in the darkness prior to analysis. Stock plant extract was prepared by an aqueous maceration and was performed on 0.2 g of plant with 100 mL of 1M HCl solution for 24 h. After filtration, the extract was recovered. The experiments were performed with mild steel with the following composition table 2. Samples were polished with emery paper up to 1200 grade, and then washed with double-distilled water, and degreased with ethanol.

C	Si	P	Al	Mn	S	Fe
0.21%	0.38%	0.09%	0.01%	0.05%	0.05%	balance

0.2. Weight loss measurements

The experiments were carried out in solution of 1.0 M HCl on mild steel. Sheets with dimensions 2.5 x 2 x 0.5 cm^3 were abraded successively with different grades of emery papers up 1200 grade, washed with distilled water, degreased with acetone, dried and kept in a desiccator. After 6 h of immersion in 1.0 M HCl with and without addition of inhibitor at different concentrations, the specimens were carefully washed in double-distilled water, dried and then weighed. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. The weight loss was used to calculate the corrosion rate in milligrams per square centimeter per hour. All experiments were carried out in freshly prepared solution at constant temperatures 35, 40, 60, 70°C and 80 ± 0.1 °C using a thermostat.

0.3. Polarization and EIS measurements

The electrochemical measurements were performed using a potentiostat PGZ100 piloted by Voltamaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The working electrode (WE) in the form of disc was cut from pure iron and was embedded in polytetrafluoroethylene (PTFE) to avoid any infiltration of electrolyte then exposing only 1 cm^2 surface to the aggressive solution. The test solution was thermostatically controlled at 37 °C in air atmosphere without bubbling. All potentials were measured against SCE.

The test solution was deaerated for 30 min at E_{corr} in the cell with pure nitrogen. Gas pebbling was maintained through the experiments. Before recording the cathodic polarisation curves, the iron electrode was polarized at -800 mV/SCE for 10 min. The potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from -800 to -200 mV at a scanning rate of 1 mVs^{-1}, which are used for the determination of corrosion current by the extrapolation of anodic and cathodic Tafel lines to a point which gives log i_{corr} and the corresponding corrosion potential (E_{corr}) for each concentration of inhibitors and for the blank solution.

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at E_{corr} after

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immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 298 K. The impedance diagrams are given in the Nyquist representation.
Experiments are repeated three times to ensure the reproducibility.

RESULTS AND DISCUSSION

0.1. Tetraclinis Articulata oil analysis
Qualitative and quantitative analyses essential oils were done using GC/MS analyses. The composition of essential oil of Tetraclinis Articulata was shown in the Table 1.

Table 1: chemical constituents of Tetraclinis Articulata oil (%)

Composés	IL	Ir /apol	Ir /pol	% apol
α-Pinene	936	931	1020	2.6
Camphene	950	943	1062	0.2
Thuja-2.4(10)-diene	946	946	1121	0.1
β-Pinene	978	971	1107	0.1
Myrcene	987	982	1155	0.6
3-Carene	1010	1009	1144	0.1
p-Cymene	1015	1014	1272	0.3
Limonene	1025	1023	1199	1.4
1.8-Cineole	1024	1023	1208	0.1
g-Terpinene	1051	1047	1215	0.1
p-Cymenene	1075	1072	1435	0.1
Terpinolene	1082	1078	1287	0.2
a-Campholenal	1105	1103	1499	1.3
Camphor	1123	1120	1527	22.8
p-Mentha-1.5-dien-8-ol	1127	1129	1602	1.4
Borneol	1150	1150	1702	24.8
p-Cymen-8-ol	1169	1167	1837	1.5
Terpinen-4-ol	1164	1162	1595	0.9
Myrtenal	1172	1169	1629	0.9
α-Terpineol	1176	1174	1700	1.2
Verbenone	1183	1181	1704	5.0
trans-Carveol	1200	1198	1826	2.1
Carvone	1214	1212	1729	0.8
Bornyl acetate	1270	1275	1591	11.4
a-Terpinyl acetate	1335	1336	1663	1.4
a-Copaene	1379	1377	1449	0.1
a-Gurjunene	1413	1405	1543	0.2
trans-Caryophyllene	1421	1414	1565	0.7
a-Humulene	1455	1444	1670	0.2
g-Muurolene	1474	1473	1656	0.7
g-Cadinene	1507	1500	1756	0.4
d-Cadinene	1520	1515	1756	0.4
Caryophyllene oxyde	1578	1570	1968	2.1
b-Oplopenone	1595	1590	2020	0.3
1-10-diepi-Cubenol	1615	1611	2049	1.1
tau Cadinol	1633	1629	2151	0.9
a-Cadinol	1643	1639	2225	0.7
			TOTAL	89.2

0.2. Effect of concentration
0.2.1. Weight loss. corrosion rates and inhibition efficiency
Gravimetric measurements of steel were investigated in 1M HCl in the absence and the presence of various concentrations of TCE and TCO at 6 h of immersion and 308 K. The following equation was used to determine the inhibition efficiency ($E_w\%$):

$$E_w \% = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \qquad (1)$$

where W_{corr} and W'_{corr} are the corrosion rate of steel in 1M HCl in the absence and the presence of inhibitor, respectively.

Table 2 summarizes the gravimetric trends of the steel immersed in aerated molar HCl in the absence and the presence of the inhibitors at various concentrations.

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It is clear that the corrosion rate decreases with the increase of concentration of the tested inhibitors and in turn the inhibition efficiency (Ew%) increases to attain 90% and 80% for TCE and TCO (at 2g/L) respectively. These results reveal that the compounds under investigation are fairly efficient inhibitors for C-steel dissolution in 1M HCl solution.

Table 2. Gravimetric results of mild steel in acid solutions 1M HCl at different concentration of TCE & TCO (308 K & 6 h)

Compounds	Concentrations (g/l)	W (mg.cm^{-2}.h^{-1})	E %
Blank	1M	0.520	-
Tetraclinis Articulata oil	0.25	0.249	52
	0.5	0.208	60
	1	0.187	64
	2	0.100	**80**
Tetraclinis Articulata extract	0.25	0.260	50
	0.5	0.197	62
	1	0.110	78
	2	0.050	**90**

0.2.2. Polarization curves

Polarization study has been carried out in order to gain knowledge about the kinetics of the anodic and cathodic reactions. Potentiodynamic curves are obtained in the presence and the absence of the studied inhibitors, after pre-polarizing the electrode at its E_{corr} for 30 min, thereafter pre-polarized at -800 mV for 10 min. After this scan, the potential was swept stepwise from the most cathodic potential to the anodic direction.

Potentiodynamic polarisation curves of steel in 1M HCl in the presence and the absence of the tested inhibitors are shown in Figs 1.
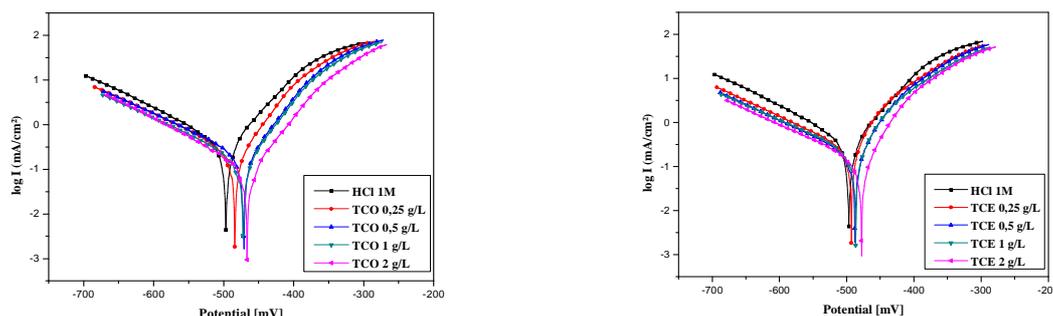
Figure 1. Cathodic and Anodic polarisation curves of mild steel in 1M HCl in the presence of Tetraclinis Articulata oil and extract at different concentrations

The corrosion parameters including corrosion current densities (I_{corr}), potential (E_{corr}), cathodic Tafel slope (β_c) and inhibition efficiency (E_I %) are listed in Table 3. In this case, the inhibition efficiency is defined as follows:

$$E_I \% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad (2)$$

where I_{corr} and I'_{corr} are, respectively the uninhibited and inhibited current density respectively. The corrosion current density was calculated from the intersection of cathodic and anodic Tafel lines. As it can be seen from Table 3 The E_{corr} values were shifted slightly toward the positive in the presence of the inhibitors in comparison to that in its absence, and the values of corrosion potential nearly remain constant with the addition of different concentration. These results indicate that TCO and TCE act as mixed-type inhibitors with predominant anodic effectiveness. According to Ferreira and others [40, 41], if the displacement in E_{corr} values (i) >85 mV in inhibited system with respect to uninhibited, the inhibitor could be recognized as cathodic or anodic type and (ii) if displacement in E_{corr} is <85 mV, it could be recognized as mixed-type. For studied inhibitors, the maximum displacement range was 31 mV towards anodic region, which indicates that the studied TCO and TCE are mixed-type inhibitors.

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Table 3. Electrochemical parameters of steel at various concentrations of TCE and TCO respectively in 1M HCl and the corresponding inhibition efficiency

Inhibitors	Concentrations (g/l)	E_{corr} (mV)/SCE	b_c (mV/dec)	I_{corr} (mA/cm^2)	E%
Blank	1M	-497	-145	0.5246	-
Tetraclinis Articulata oil	0.25	-483	-142	0.2419	53
	0.5	-472	-142	0.1933	63
	1	-471	-135	0.1816	65
	2	-466	-111	0.1214	**76**
Tetraclinis Articulata Extract	0.25	-483	-142	0.2734	48
	0.5	-471	-135	0.1992	62
	1	-466	-111	0.1214	76
	2	-466	-111	0.0700	**86**

The cathodic Tafel slopes were found to vary over a range of 111-145 mV dec^{-1} .Therefore, the cathodic slope value was found to change with increasing concentration of TCO and TCE in 1 M HCl. This result indicates the influence of the inhibitor on the kinetics of the hydrogen evolution reaction.

The electrochemical parameter values given in Table 3 reveal that inhibition efficiency increases with an increase of the concentration of inhibitors. We remark that the corrosion current densities were more significantly reduced in the presence of TCE than TCO. The best efficiencies obtained in the presence of TCE and TCO respectively are 86% at and 76g/L at 2g/L.

0.3. Electrochemical impedance spectroscopy measurements

The corrosion behavior of steel in 1M HCl solution, in the absence and the presence of TCO and TCE, is also investigated by the EIS at 303 K after 30 min of immersion. Nyquist plots of mild steel in uninhibited and inhibited acid solutions containing different concentrations of TCO and TCE are presented in Figure 2. It can be observed from Fig 2 that the size of the capacitive semicircle in the presence of inhibitors is larger than the size of the capacitive semicircle in the absence of these inhibitors. This fact is attributed to the inhibition effects of Tetraclinis Articulata inhibitors. Table 4 shows the charge-transfer resistance (R_t) values which are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [42], 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:

$$C_{dl} = \frac{1}{2\pi . f_m . R_t}$$ (3)

With C_{dl} : Double layer capacitance (µF.cm^{-2}) ; f_m : maximum frequency (Hz) and R_{ct} : Charge transfer resistance (Ω.cm^2).
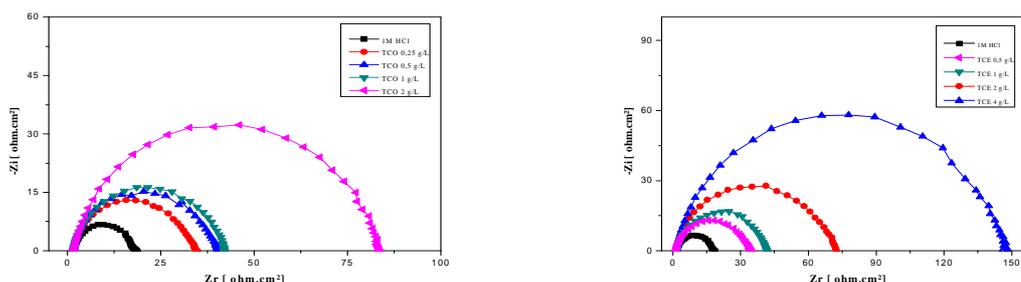
Figure 2. Nyquist diagrams for steel electrode with and without Tetraclinis Articulata after 30 min of immersion

Table 4. Impedance parameters for corrosion of steel in acid at various contents of TCO and TCE respectively

Inhibitors	Concentrations(g/l)	R_t (Ohm.cm^2)	f_{max} (Hz)	C_{dl}(µF.cm^{-2})	E%
Blank	1M	16.51	-	-	-
Tetraclinis Articulata oil	0.25	33.09	125	38	50
	0.5	38.14	100	41	56
	1	40.35	100	39	60
	2	81.85	40	48	**80**
Tetraclinis Articulata extract	0.25	32.06	125	38	48
	0.5	39.76	79	41	58
	1	70.39	50	45	76
	2	174.5	20	45	**88**

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Table 4 embodies various parameters such as R_t, double layer capacitance (C_{dl}) and E_R %. It was observed that the values of inhibition's efficiency increase with inhibitor concentration at a maximum value 88% and 80% for TCE and TCO respectively at 2g/L. The adsorption of inhibitive molecules on the metal /surface and the decrease of its roughness can be justified by the gradual variation in values of C_{dl} from 38 to 48 µF.cm^{-2} at different concentrations. The values of E_R % were calculated by the equation as follows:

$$E_R\% = \frac{R'_t - R_t}{R'_t} \times 100 \tag{4}$$

0.4. Effect of temperature
0.4.1.Kinetic parameters
The effect of temperature on inhibition reaction is highly complex, because many changes may occur on the metal surface such as rapid etching, rupture, desorption of inhibitor and the decomposition and/or rearrangement of inhibitor. However, it provides the ability of calculating many thermodynamic functions for the inhibition and/or the adsorption processes which contribute to determining the type of adsorption of the studied inhibitors [43]. In order to determine the activation energy of the corrosion process, and to gain more information about the type of adsorption and the effectiveness of the studied inhibitors at higher temperatures, gravimetric experiments were performed at different temperatures (313–343 K) for the steel electrode in 1 M HCl in the absence and the presence of TCE and TCO at 2g/L. The corresponding results are given in Table 5.

Table 5. Inhibition efficiency obtained from the corrosion rate at 2g/L of different inhibitors in 1 M HCl at different temperature at 1h immersion period.

T(K)	Blank W	TCE W	TCE E%	TCO W	TCO E%
313	0.89	0.17	80.8	0.20	76.8
323	1.35	0.34	74.6	0.47	65.3
333	2.85	0.79	64.8	1.36	52.1
343	5.83	1.39	62.5	3.73	35.9

As seen in Table. 5 that in the absence and the presence of different inhibitors the increase of corrosion rate is more pronounced with the rise of temperature and the inhibition efficiency decreases to reach a value of 36% and 62% at 343 K for TCO and TCE respectively at 1h immersion period. It is clear also, that the corrosion rate W_{corr} in the presence of CAO and TCE is highly reduced even at high temperature. We note also that the inhibition efficiency decreases slightly with temperature. This can be justified by the decrease of the strength of adsorption processes at high temperature and suggested a physical adsorption mode [44]. From this result, we can deduce that TCO and TCE are excellent inhibitors. The activation energies for the corrosion process were calculated from the Arrhenius equation (5):

$$W = A.\exp\left(-\frac{E_a}{R.T}\right) \tag{5}$$

where E_a represents the apparent activation energy, R gas constant, T the absolute temperature, A the pre-exponential factor and W the corrosion rate, obtained from the weight loss method.
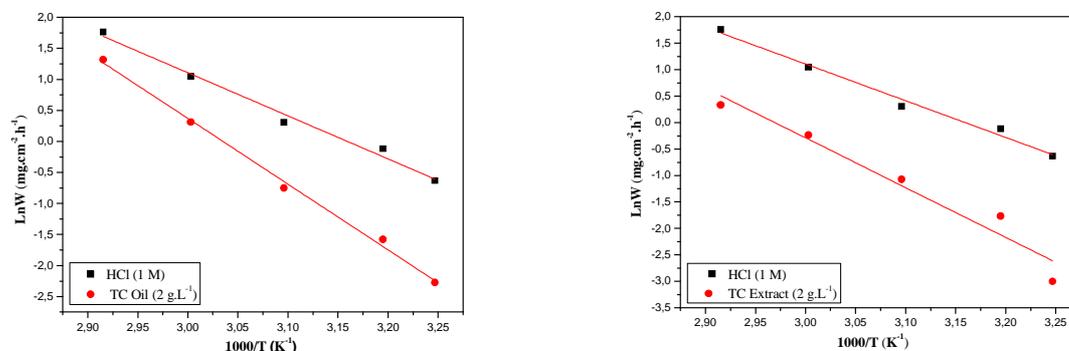
Figure 3. Arrhenius plots of steel for 2 g/L of TCE and TCO in 1 M HCl

Arrhenius plots for the corrosion rate of mild steel are given in Figure 3. Values of E_a for mild steel in 1M HCl in the absence and the presence of various concentrations of TCE and TCO were determined from the slopes of ln

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(W) versus 1000/T plots. The activation energy values obtained are 88, 78 and 57 kJ/mol for 2g/L of TCO, TCE and free acid, respectively. It's seen that E_a increases slightly in the presence of TCO and TCE that indicates the good performance of these inhibitors at higher temperatures. Generally, the addition of compounds to the corrosive solution is accompanied by an increase in activation energy value when compared to the blank, which may often be interpreted as an indication for the formation of an adsorptive film by a physical (electrostatic) mechanism [45, 46].
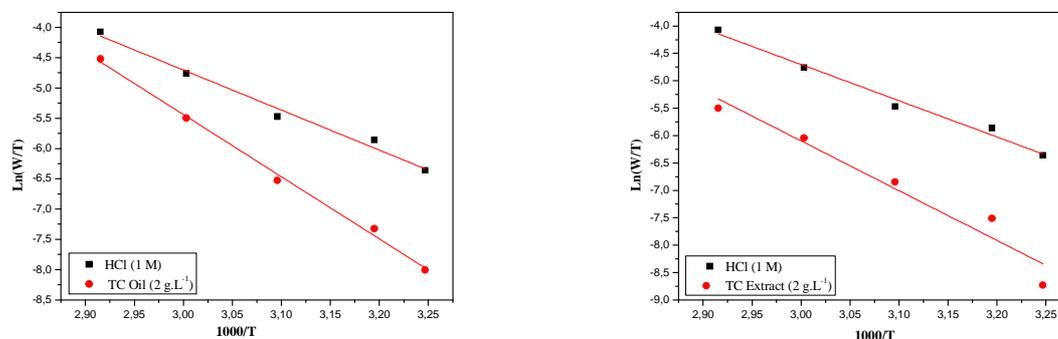

Figure 4. The variation of Ln (W / T) ~ f (1000 / T) of the steel in 1M HCl with and without TCE and TCO

Kinetic parameters, such as enthalpy (ΔH_a^o) and entropy (ΔS_a^o) activation energies may be evaluated by the alternative formulation (eq. 6). where W refers to the corrosion rate, R the gas constant, T the absolute temperature, A the pre-exponential factor, h is Plank's constant and N is Avogadro's number

$$W = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^o}{R}\right)\exp\left(-\frac{\Delta H_a^o}{RT}\right) \tag{6}$$

Figure 4 shows the plots of ln(W/T) versus 1000/T. Straight lines are obtained with a slope of ($-\Delta H_a^o/R$) and an intercept of (Ln (R/Nh) $+ \Delta S_a^o/R$). The calculated values of ΔH_a^o, ΔS_a^o and ΔG_a^o are collected in Table 6.

Table 6. Activation parameters for steel in 1M HCl in the absence and presence of TCE and TCO

Inhibitors	$\Delta H_a\ k\ j.mol^{-1}$	$\Delta S_a\ j.K^{-1}.mol^{-1}$	$\Delta G_a\ (k\ j.mol^{-1}\ at\ 298\ K)$
Blank	55	-71	76
TCO	85	-13	81
TCE	75	-21	81

From the results obtained in Table 6, it can be concluded that:

• The positive signs of the enthalpies (ΔH_a^o) reflect the endothermic nature of the steel dissolution process (Table 6).

• Large and negative values of entropies (ΔS_a^o) 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 reactants to the activated complex and suggesting that the dissolution reaction will be more blocked sites from the metal surface [47].

• The ΔG_a values for inhibited systems were more positive than that for the uninhibited systems, revealing that in the presence of the added inhibitor, the complex of the activated corrosion becomes less stable as compared to its absence.

0.4.2. Adsorption isotherm
Adsorption isotherms are usually used to describe the behavior of the inhibitor on the electrode surface. Among several adsorption isotherms which tested the Langmuir adsorption isotherm was found to provide best description of the adsorption behavior of the investigated inhibitor. The Langmuir isotherm is given by the equation [48]:

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$$\frac{C}{\theta} = \frac{1}{K} + C \tag{7}$$

With $K = \frac{1}{55.5}.\exp\left(-\frac{\Delta G_{ads}}{R.T}\right)$ (8)

Where C is the inhibitor concentration, θ the fraction of the surface covered determined by E%/100, k the equilibrium constant, ΔG_{ads} is the standard free energy of adsorption reaction, R is the universal gas constant, T is the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution in mol/L. Figs. 5 and 6 show the dependence of the ratio C/θ as function of C for TCE and TCO respectively.
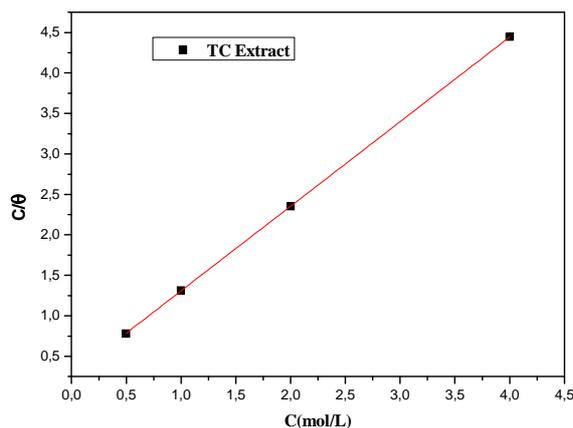

Figure 5. Plots of Langmuir adsorption isotherm of TCE on the steel surface at 298K

A straight line was obtained by plotting the graph of C vs C/θ with the R value almost unity (0.9999) (Fig 5). The slope is reported almost unity suggesting that the Langmuir adsorption isotherm model provides the best description of the adsorption behavior.
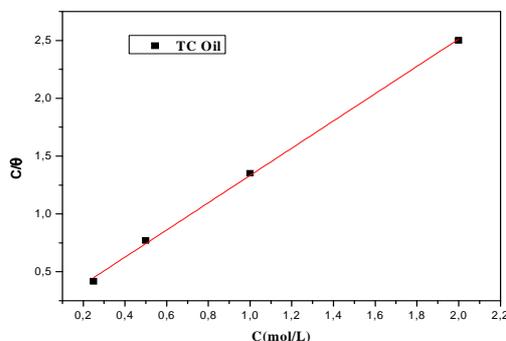

Figure 12. Plots of Langmuir adsorption isotherm of TCO on the steel surface at 298K

CONCLUSION

In this work, we have studied the corrosion inhibition of Tetraclinis Articulata oil and extract for mild steel in 1M HCl solution by gravimetric method and electrochemical techniques such as potentiodynamic polarization. The results obtained are in good agreement and are given as follows:

o The analysis of essential oil isolated from Tetraclinis Articulata plant shows that its composition is dominated by Camphor, Borneol and Bornyl acetate (22.8%, 24.8% and 11.4%, respectively).
o TCE and TCO act as mixed-type inhibitors without modifying the mechanism of hydrogen evolution.
o The adsorption onto the carbon steel surface was characterized by the decrease in the cathodic and anodic current densities observed in the potentiodynamic polarization curves carried out in the presence of TCE and TCO

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o The inhibition efficiency of TCE and TCO increases with the increase of inhibition concentration to reach 90% at 2g/L of TCE and 80% at 2g/L of TCO.

o The data obtained from the three different methods: potentiodynamic polarization, EIS and weight loss have the same tendency.

o The inhibition efficiency of TCE and TCO decreases with the rise of temperature.

o Adsorption of the inhibitor molecules on the metal surface fits Langmuir adsorption isotherm model

o TCE and TCO being natural and environmentally benign products, they can be used as an alternative for toxic chemical inhibitors in acidization and acid pickling of mild steel.

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