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Inhibition of Steel Corrosion in 1 M HCl by the Essential Oil of Thymus pallidus

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ABSTRACT

The composition of the essential oil isolated from the aerial parts of Thymus pallidus an endemic plant from Morocco was investigated by GC and GC/MS. The oil of T. pallidus was found to be rich in monoterpenes hydrocarbons, with borneol (36.6%) being the major component. The effect of Thymus pallidus essential oil extract as a corrosion inhibitor on the corrosion rate of Carbon Steel (CS) in hydrochlorid acid environment was investigated using gravimetric method potentiodynamic polarizations and electrochemical impedance spectroscopy (EIS) methods. The corrosion rates were studied in different concentrations of T. pallidus oil at 298 K. The results revealed that T. pallidus oil in acid environment decreased the corrosion rate at various concentrations considered. The maximum inhibition efficiency of 88.65 % was achieved with 1.0 g/l inhibitor concentration at 298K. Polarization measurements show also that T. pallidus oil act as good mixed inhibitor. The results demonstrated that T. pallidus oil adsorbed on the surface of carbon steel and obeyed Langmuir adsorption isotherm.

Keywords: Corrosion; Steel; Inhibition; essential oil composition; Acid medium; Thymus pallidus; borneol.

INTRODUCTION

Corrosion is due to an electrochemical or chemical action of the environment on metals and alloys. This has important implications in various fields, especially in industries. Replacement of corroded parts, accidents and pollution risks are frequent events which sometimes have severe economic impacts. The use of inhibitors is a practical technique to secure metals and alloys from aggressive environment. Large numbers of organic compounds revealed that N, S and O containing organic compounds may be efficient inhibitors. However, these products are generally obtained by chemical synthesis and therefore have a negative impact on the environment. This has led many researchers around the world to use new non-polluting natural molecules to the environment. Otherwise; most of these compounds are not only expensive, but also toxic to living beings. It is needless to point out the importance of cheap and safe inhibitors of corrosion. So, considerable efforts are made to find alternative environmentally ecofriendly acid corrosion inhibitors, ready available and of relatively low cost. Literature shows a growing trend in the use of natural products known as non-toxic compounds, called also green inhibitors, as corrosion inhibitors. In addition, several studies have been made to study the inhibitory effect of various natural substances against the corrosion of materials, particularly in the steel industry: extract Khillah [1], Thymelia hursuta Endl [2], opuntia extract [3], Artemisia [4-6], Black Pepper Extract

[7], Eugenol and Acetyleugenol [8], Ginger [9], Limonene [10], Argania plant extract [11] and. Natural plants are added as extract, oil of natural plants are the subject of various contributions: Prickly pear seed oil extract [12], Menthols [13], Rosemary oil [14-16], oil of L. angustifolia Lavender [17], essential oil of cedar [18], Thymus oil [19-20], oil of wormwood [21-23], Lavender oil [24], Chamomile oil [25], Jojoba oil [26]; Pennyroyal Mint oil [27], Argan oil [28], Argania spinosa Kernels Extract and Cosmetic Oil [29], eucalyptus oil [30,31] and thymus oil [32],Verbena Essential Oils[33]. The aim of this study was to determine the chimecal composition of *Thymus pallidus* essencial oil extract in Morocco, and to study the inhibitive action of *T. pallidus* as a eco friendly and naturally occurring substance on corrosion behaviour of Carbon steel in 1M HCl by gravimetric measurements method and electrochemical techniques such as potentiodynamic polarisation, linear polarisation and electrochemical impedance spectroscopy (EIS).

MATERIALS AND METHODS

2.1.Plant collection and essential oil isolation

The plant was collected in the region of Agadir, Morocco. It was taxonomically identified at the National Scientific Institute of Rabat (Department of Plant Biology, Laboratory of Botany). The plant aerial parts used for essential oil isolation were separately air-dried and ground. From the powder a sample of 200 g was subjected to water distillation for 2h using a Clevenger-type apparatus recommended by the French Pharmacopoeia (1). The yield (w/w) obtained was 3.50. The oil was analyzed using a Hewlett-Pac T. kard 5972 MS, fitted with a HP 5890 Series II GC and controlled by a G1034C Chemstation. A sample of 1µL was injected under the following conditions: DB-1 fused silica capillary column (20 m x 0.20 mm, film thickness 0.2 µm); carrier gas helium (0.6 mL/min); injector temperature 250 °C; column temperature 50°-250°C at 3°C/min; MS electronic impact 70 eV. The identification of the compounds was achieved by comparing retention times and mass spectra with those of the published standards [34-36]. A part of the oil after extraction was used for tests of anti-corrosion activity.

2.2. Corrosive solution

The solution 1.0 M HCl was prepared by dilution of concentrated HCl (37%) with double distilled water. The solution tests are freshly prepared before each experiment by adding the oil directly to the corrosive solution. The environment is not deaerated.

2.3. Weight loss measurements

Coupons were cut into 2 × 2 × 0.08 cm^3 dimensions are used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers. The specimens were washed thoroughly with bidistilled water, degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 80 mL. The immersion time for the weight loss is 6 h at 298 K.

2.4. Polarization measurements

2.4.1.Electrochemical impedance spectroscopy (EIS)

The electrochemical measurements were carried out using Volta lab (PGZ 100) potentiostate and controlled by software model (Voltamaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode. The working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to a establish steady state open circuit potential (Eocp). After measuring the Eocp, the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 298 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x-axis.

2.4.2. Potentiodynamic polarization

The electrochemical behaviour of carbon steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 1.0 M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -800 mV to -200 mV versus corrosion potential at a scan rate of 1 mV. s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (Icorr).

RESULTS AND DISCUSSION

3.1. Analyzing the chemical composition of the essential oil

The results of GC/MS analyses of hydro-distillated essential oil of *Thymus pallidus* allowed the identification of 25 different components in the oil, representing 96.3.0% of the compounds in the oil (Table 1). According to the analysis results, borneol was the most abundant component of the oil (36.6 %). Other main components of the oil were camphre (18.9%), α-terpineol (10%), camphene (6.3%), γ-terpinene (4.1%) and β-caryophyllene (3.2%).

Table 1: Chemical composition (%) of the *Thymus pallidus* essential oil extract.

Compound	KI	T. pallidus essential oil (%)
Tricyclene	926	0.4
α-pinene	939	2.4
β-pinene	980	0.8
Camphene	983	6.3
Myrcene	991	0.6
1,8-cineole	1032	0.9
γ-terpinene	1062	4.1
allo-ocimene	1088	0.4
Camphre	1143	18.9
Borneol	1165	36.6
Terpinen-4-ol	1175	2.9
α-terpineol	1189	10.0
Bornyl acetate	1285	2.0
Thymol	1290	1.3
Carvacrol	1298	0.9
β-caryophyllene	1418	3.2
Germacrene D	1485	1.0
Bicyclogermacrene	1500	0.3
γ-cadinene	1513	0.4
δ-cadinene	1523	0.3
Spathulenol	1572	0.4
Caryophyllene oxyde	1583	0.9
α-muurolol	1646	0.7
α-cadinol	1650	0.4
α-humulene	1709	0.2
Total monoterpenes		88.5
Total sesquiterpenes		7.8
Total of identified componds		96.3
Yield		3.5

KI: Kováts indices

1.1. Electrochemical impedance spectroscopy measurements (EIS)

The corrosion behavior of steel 1.0M HCl solution with and without *T. pallidus* essential oil is also investigated by the electrochemical impedance spectroscopy (EIS) at 298K after 30min of immersion. The charge transfer resistance (R_{ct}) values are calculated by subtracting the high frequency intersection from the low frequency intersection **[37]**. Values of the charge transfer resistance R_{ct} were obtained from these plots by determining the difference in the values of impedance at low and high frequencies [38].

Double layer capacitance C_{dl} values were obtained at maximum frequency (f_{max}), at which the imaginary component of the Nyquist plot is maximum and calculated using the following equation:

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

With C_{dl}: Double layer capacitance (µF.cm^{-2}); f_{max}: maximum frequency (Hz) and R_{ct}: Charge transfer resistance (Ω.Cm^2).

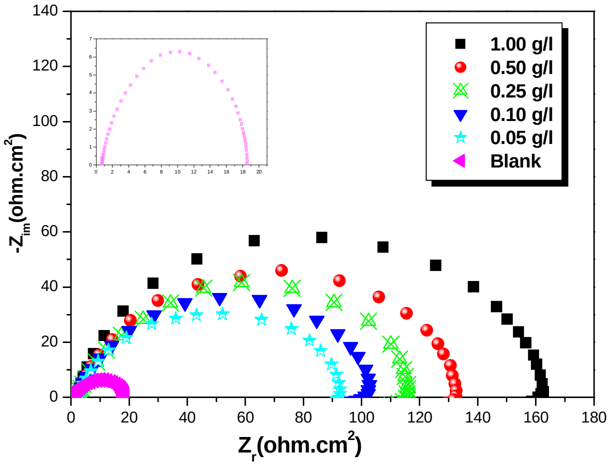

Figure 1. Nyquist plots for the corrosion of Carbon steel in 1.0 M HCl containing different concentrations of *Thymus pallidus* oil extract at 298K.

Impedance diagrams are obtained for frequency range 100 KHz–10 mHz at the open circuit potential for Carbon steel in 1.0 M HCl in the presence and absence of *T. pallidus* essential oil extract. Nyquist plots for carbon steel in acid medium at various concentrations of *T. pallidus* oil extract is presented in Fig.1. Table 2 gives values of charge transfer resistance R_{ct}, double layer capacitance Cdl, and fmax derived from Nyquist plots and inhibition efficiency, the inhibition efficiency got from the charge transfer resistance is calculated by the following equation:

$$E_{Rct}\ \% = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100 \qquad (2)$$

Where R_{ct} and R'_{ct} are the charge transfer resistance values without and with inhibitor, respectively.

Generally, Fig.1 showed that the impedance spectra reveal a similar semicircle shape of the curves, the shape is maintained throughout the whole concentration, indicating that almost no change in the corrosion mechanism occurred due to the inhibit or addition of inhibitor [39] and the diameters of semicircles increases with the inhibitor concentration. The obtained impedance diagrams show semi-circular appearance that can be attributed to the charge transfer that takes place at electrode/solution interface and the transfer process controls the corrosion reaction of carbon steel and the presence of inhib itor does not change the mechanism of dissolution of steel [40, 41] It is also clear that these impedance diagrams consists of one large capacitive loop and they are not perfect semicircles and Deviations of perfect circular shape are often refereed to the frequency dispersion of interfacial impedance. This anomalous phenomen on is interpreted by the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena [42, 43].

Table 2. Electrochemical Impedance parameters for corrosion of steel in acid medium at various contents of *Thymus pallidus* oil extract.

Inhibitors (g/l)	R_t(kΩ.cm^2)	f_{max}(Hz)	C_{dl}(µF/cm^2)	E_{RT} (%)
0.00	18	40	221.16	-
1.00	160	40	24.88	88.75
0.50	132	63	19.15	86.36
0.25	116	75	18.30	84.48
0.10	101	90	17.52	82.18
0.05	92	100	17.31	80.43

From the inspecting of Table 2 data, we notice an increase of the polarization resistance R_{ct} and decrease of the double layer capacitance C_{dl} with increasing inhibitor concentration indicate that *T. pallidus* oil extract inhibits the corrosion rate of mild steel by an adsorption mechanism **[44].** The efficiency reaches 88.75% at 1g/L .Values of double layer capacitance are also brought down to the maximum extent in the presence of the inhibitor, the decrease being more effective with rise of concentration, and the decrease in the values of C_{dl} follow the order similar to that obtained for the I_{corr} studies. The decrease in C_{dl} is due to the adsorption of this compound on the metal surface leading to the formation of a surface film in the acidic solution **[45].**

The results obtained from the polarization technique in acidic solution were in good agreement with those obtained from the electrochemical impedance spectroscopy (EIS) with a small variation.

1.2. Polarization curves

The Tafel curves of Carbon steel both in presence and absence of various concentrations of the essential oil of *T. pallidus* in 1 M HCl were shown in Fig. 2. The electrochemical parameters such as corrosion potential E_{corr}, corrosion current density I_{corr}, inhibition efficiency E_I *(%)* and tafel constants bc obtained from cathodic curves were listed in Table 3. From the results inhibitor predominantly inhibits cathodic reaction.

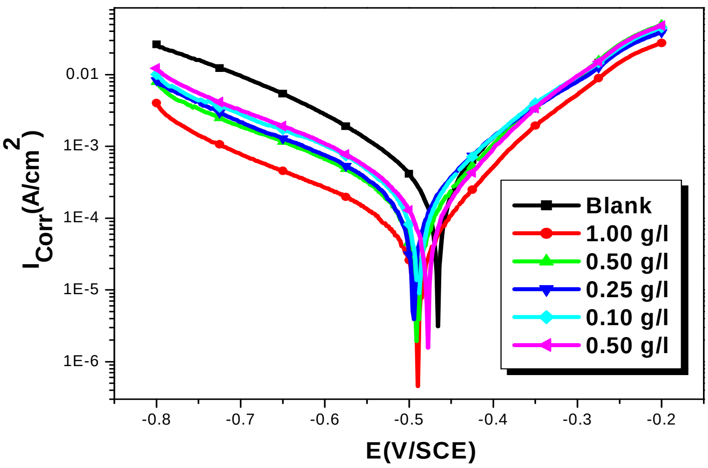

Figure 2. Polarization curves of Carbon steel in 1.0 M HCl in the presence of differents concentration of *Thymus pallidus* essential oil at 298K of the corrosive medium.

It was observed that the current density increased along with the inhibitor concentration indicating the increase in corrosion rate. As seen from Fig. 2, the inhibitor affects both anodic and cathodic reactions. The cathodic effect is then dominant against the anodic one. In the other hand in the anodic domain, a slight decrease of anodic current is observed in the presence of natural product. We remark also that cathodic current potential curves give rise to parallel Tafel lines indicating that the hydrogen evolution reaction is activation controlled and the addition of the inhibitor studied does not modify the mechanism of this process [45]. The observed inhibitory action of *T. pallidus* essential oil may be due to the adsorption of its molecules on the metal surface, making a barrier for the access of hydrogen ions, and then their reduction on the cathodic sites of the steel surface [47].

Table 3. Electrochemical parameters of C-steel at various concentrations *Thymus pallidus* oil extract in 1M HCl and corresponding inhibition efficiency.

Inhibitors (g/l)	$-E_{corr}$(mV/SCE)	I_{corr}(μA/cm^2)	$-b_c$ (mV/dec)	E_I (%)
0.00	465	588	168	-
1.00	492	71	198	87.92
0.50	493	83	190	85.88
0.25	494	107	179	81.80
0.10	492	123	194	79.08
0.05	485	165	166	71.94

The percentage inhibition efficiency values E_I(%), were calculated using equation:

$$E_I \ \% \ = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad (3)$$

where I_{corr} and I'_{corr} are current density in absence and presence of *T. pallidus* essential oil extract respectively. We noted that I_{corr} and I'_{corr} were calculated from the intersection of cathodic and anodic Tafel lines.

The inspection of results in table 1 indicate that *T. pallidus* essential oil extract inhibits the corrosion process in the studied range of concentrations and E_I (%) increases with C_{inh}, reaching its maximum value, 87.92%, at 1.0

g/l. However, at potentials higher than -240 mV/s, the presence of *T. pallidus* essential oil extract shows no effect on the anodic curves. This feature of the current is associated with the development of localized corrosion. These results suggest that the inhibitory action depends on the potential of *T. pallidus* essential oil extract and adesorption process appears at high potential [48]. These results suggest that this compound acts as a good corrosion inhibitor mixed character with a strong predominance of anodic character [49]. These polarization curves tests were in good agreement with the corrosion weight loss and impedance measurements.

1.3. Weight loss measurement and adsorption isotherm

The corrosion rate Wcorr of steel in 1.0M HCl solution at various contents of *Thymus pallidus* essential oil tested was determined after 6h of immersion period at 298K. Values of corrosion rates and inhibition efficiencies are given Table 4. In the case of the weight loss method, the inhibition efficiency E_w % and surface coverage (θ) were determined by using the following equations:

$$E_w \% = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \quad (4)$$

$$\theta = 1 - \frac{W'corr}{Wcorr} \quad (5)$$

Where Wcorr and W'corr are the corrosion rates of Carbon steel due to the dissolution in 1M HCl in the absence and the presence of definite concentration of inhibitor, respectively, and θ is the degree of surface coverage of the inhibitor.

Table 4: Weight loss data of carbon steel in 1.0 M HCl for various concentration of the *Thymus pallidus* essential oil.

Inhibitors (g/l)	Wcorr (mg .cm^{-2} .h^{-1})	Ew(%)	θ
0.00	1.1001	---	---
1.00	0.122	87.81	0.88
0.50	0.143	85.71	0.86
0.25	0.161	83.91	0.84
0.10	0.192	80.82	0.81
0.05	0.211	78.92	0.79

The analysis of these results Table 4 shows clearly that the corrosion rate decreases W_{corr} while the inhibition efficiency E_w% increases with increasing inhibitor concentration reaching a maximum value of 87.81% at a concentration of 1g/l. This behavior can be attributed to the increase of the surface covered θ, and that due to the adsorption of ecofriendly compounds on the metal surface, as the inhibitor concentration increases. We can conclude that *Thymus pallidus* essential oil is a good ecofriendly corrosion inhibitor for steel in 1.0 M HCl solution. Basic information on the interaction between the inhibitor and the steel surface can be provided by the adsorption isotherm. The adsorption isotherms are very important for understanding the mechanism of the electrochemical reactions of metals [50]. Knowledge of the type of adsorption and the determination of the thermodynamic parameters characterizing the adsorption often helps to elucidate the mode of action of these inhibitors. In order to obtain the isotherm, the linear relation between degree of surface coverage (θ) values (Table 4) and inhibitor concentration (Cinh) must be found. The most frequently used isotherms are Langmuir, Frumkin and Temkin ones [51]. By far the best fit is obtained with the Langmuir isotherm. This model has also been used for other inhibitor systems [52, 53]. According to this isotherm, Cinh/ θ is related to C_{inh} by:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (6)$$

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (7)$$

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.

Fig. 3 shows the dependence of the ratio C/ θ as function of C.

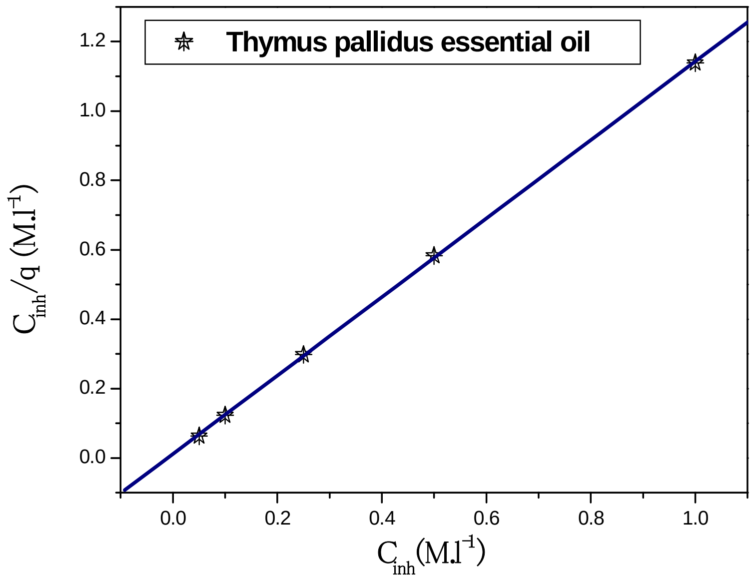

Figure 3: plots of Langmuir adsorption isotherm of *Thymus pallidus* essential oil extract on the steel surface at 298k.

The strong correlations (R^2 = 0.99994 confirm the validity of this approach. The values of Kads obtained from the Langmuir adsorption isotherm are listed in Table 5, together with the values of the Gibbs free energy of adsorption calculated from the equation:

$\Delta G_{ads} = - RTLn\ (55.5Kads)$ (8)

Where R is the universal gas constant, T the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution [54].

Table 6. Thermodynamic parameters for the adsorption of *T. Pallidus* oil extract in 1M HCl on the carbon steel at 298K.

Inhibitor	Slope	$K_{ads}\ (M^{-1})$	R^2	ΔG°_{ads} (kJ/mol)
T. pallidus oil	1.13	84.80	0.99	-20.942

The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on carbon steel surface. From Eq. (8), ΔG_{ads} was calculated as -20.94 kJ mol^{-1} for *Thymus pallidus* essential oil. The negative value of standard free energy of adsorption indicates spontaneous adsorption of our molecule on carbon steel surface and also the strong interaction between inhibitor molecule and the metal surface [55, 56]. Generally, the standard free energy values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption); those of - 40 kJ mol^{-1} or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [57, 58].The value of ΔG_{ads} in our measurement is -20.94 kJ mol^{-1} for it is suggested that the adsorption involves the physisorption interactions.

CONCLUSION

We have studied the inhibiting effect of *Thymus pallidus* essential oil after chracterisation in 1.0 M HCl on the steel by using various methods. The results obtained are in good agreement and can be summarized as follows:

- Chemical analysis shows that the major constituents of *Thymus pallidus* essential oil were borneol was the most abundant component of the oil (36.6 %), camphre (18.9%) and α-terpineol (10%).
- The *T. pallidus* oil provides a good inhibition of corrosion of steel in normal hydrochloric acid medium.
- Weight-loss data showed that the presence of *T. pallidus* oil significantly inhibit the severe steel corrosion in HCl solutions: this effect increases with the increase of their concentrations.

 Potentiodynamic polarization measurements indicated that the increased concentrations of *T. pallidus* oil affect both anodic and cathodic reactions.
 EIS measurement results indicated that the resistance of the carbon steel electrode increased greatly and its capacitance decreases by increasing the inhibitor concentration.
 The inhibition efficiency increases with increased *Thymus pallidus* essential oil concentration to attain a maximum value of 88.75 % at 1g/l.
 Results together are internally consistent with each other, showing that *T. pallidus* oil is a good corrosion inhibitor for copper in 1.0 M HCl; it inhibit the corrosion by the strong adsorption of their molecules on the steel surface.
 The *T. pallidus* oil acts on steel surface as mixed inhibitor with a physisorption mechanism.

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