J. Mater. Environ. Sci. 7 (11) (2016) 3949-3960 *Salhi et al.*
ISSN : 2028-2508
CODEN: JMESCN

Chemical composition, antioxidant and anticorrosive activities of Thymus Algeriensis

A. Salhi[1,*], A. Bouyanzer[1], I. El Mounsi[2], H. Bendaha[2], I. Hamdani[1], E.El Ouariachi[1],A. Chetouani[1,3], N. Chahboun[4], B. Hammouti[1], J.M. Desjobert[5], J. Costa[5]

[1] *LCAE-URAC18. Faculté des Sciences. Université Mohammed Premier. B.P. 4808. 60046 Oujda. Morocco*
[2]*Laboratoire de la chimie des matériaux (LCM), Facul té des Sciences, Université Mohammed Premier, Oujda, Morocco*
[3] *Laboratoire de chimie physique, Centre Régionale des Métiers de l'Education et de Formation "CRMEF", Région de l'Orientale, Oujda, Morocco.*
[4] *Laboratoire de Biotechnologie, Environnement et Qualité (LABEQ), Département de Biologie, Faculté des Sciences, Université Ibn Tofaïl, BP 133, 14000 Kenitra, Morocco.*
[5] *UMR CNRS 6134. Lab. de Chimie des Produits Naturels. Université de Corse. France*

Received 07 Apr 2016, Revised 10 Aug 2016, Accepted 25 Aug 2016
**Corresponding author. E-mail: amiinsalhii@gmail.com; Tel: (+212 642885971)*

Abstract
Known therapeutic applications of medicinal plants were made of them an alternative to synthetic compounds. In this situation, the present study was designed to give more knowledge and helping to exploit the leaves of Thymus algeriensis by determining the chemical composition of its essential oil, the phenolic content of the aqueous extract and evaluate the antioxidant and anticorrosive activity. The essential oil was characterized by Geranyl acetate (80.8%) as mainly compound. The aqueous extract has exhibited a moderate antioxidant activity against free radical DPPH. On the other hand, this work describes the successful performance of T. algeriensis as an eco-friendly corrosion inhibitor for acidic media. The corrosion inhibiting effect of the extract and the essential oil of T. algeriensis (TAE & TAO) on mild steel in 0.5 M H_2SO_4 solution was investigated by electrochemical studies in the presence of different concentrations of TAE & TAO ranging from 0.25 g/L to 2 g/L. Potentiodynamic polarization showed that TAE and TAO behaves as mixed type inhibitors. Nyquist plots show that the efficiency of inhibition increases with increasing concentration of T. algeriensis and the increased charge transfer resistance.

Keywords: Thymus algeriensis, adsorption, corrosion, green inhibitor, mild steel, sulfuric acid.

1. Introduction

In the plant kingdom, the genus Thymus belongs to the Lamiaceae family which comprises about 215 to 400 species according to numerous previous studies [1-2]. Generally, this genus consists of perennial plants and subshrubs native mainly in Europe, Western Asia and in the Mediterranean regions [3-4]. Historically, the aerial parts and the volatile constituents of Thymus species have been commonly used as herbal teas, condiments and spices. In addition, they have showed many ethnomedicinal properties such as tonic, carminative, digestive, antispasmodic, antimicrobial, antioxidant, antiviral, anti-inflammatory and various medicinal purposes [5-7].
T. algeriensis is the most pervasive North African species, endemic to Morocco, Tunisia, Algeria and Libya. In Morocco, it is encountered in the Middle Atlas, the High Atlas, the Anti Western Atlas, the Rif and the Oriental. It has a broad spectrum of biological activities [8, 12]. Throughout the history, T. algeriensis is largely used in traditional medicine, as a fresh or dry seasoning, in respiratory and digestive tube disorders and against abortion [13].
Currently, interest on the natural antioxidants concurrent and promoters has been the subject of several studies compared to previous years. Scientific researchers have focused their efforts to extract, identify and quantify the

compounds of several natural substances, including medicinal and food plants [14-16]. Another advantage is also brought to the use of these plants as a source of corrosion inhibitors against Iron and alloys.

The use of green chemical inhibitors has been acknowledged as a very practical method and an economical method of combating corrosion [17-19]. The employ of chemical inhibitors is being the most practiced methods for defending against corrosion, particularly in corrosive media [20-33].

Although the synthetic corrosion inhibitors are highly efficient, they cannot be used frequently for the purpose of corrosion inhibition because of their high operating cost and hazardous environmental effects. Recently, the restrictive environmental regulations have pushed scientists to focus their research to develop cheap, non-toxic and environmentally benign natural corrosion inhibitors [34-37]. Numerous natural products have been utilized as corrosion inhibitors to date, which are extracted from aromatic herbs, spices and medicinal plants [38-47]. Plant extracts, fruits and their peels, etc., are viewed as an incredibly rich source of natural chemical compounds which can be extracted by simple and low-cost procedures and which are biodegradable in nature. The use as corrosion inhibitors of natural compounds extracted from leaves or seeds, for example, have been widely reported by several authors [48-53].

The purpose of this work was to evaluate the antioxidant activity by the scavenging free radical DPPH method, and to evaluate the inhibitive action of T. algeriensis oil (TAO) and its extract (TAE) on corrosion behavior of carbon steel in 0.5 M H_2SO_4 using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods.

2. Experimental Details

2.1. Plant collection

The aerial parts (stalks, leaves and flowers) of T. algeriensis were harvested in June from the area of Al Hoceima National Park (Morocco) and located at 35°14'04.6"N latitude and 3°58'45.0"W longitude. The dried plant material was stored in the laboratory at room temperature and in the shade before the extraction. H_2SO_4 solutions were prepared by diluting a Merck analytical commercial grade 98 % H_2SO_4 with deionized water.

2.2. *Solution preparation*

The essential oil was extracted from the leaves parts by hydrodistillation for 3 hours using the Clevenger type apparatus according to the method recommended in the European Pharmacopoeia [54]. The oils were dried over Na_2SO_4 as a dehydrating agent and then stored prior to analysis. Stock plant extract was prepared by an aqueous maceration.

The specimens used in this study was a mild steel with a chemical composition (in wt%) of 0.09 % P, 0.38 % Si, 0.01 % Al, 0.05 % Mn, 0.21 % C, 0.05 % S, and balance Fe. These specimens were mechanically polished with emery paper up to 1200 grade, then cleaned in ultrasonic bath with ethanol, rinsed with bidistilled water and finally dried at room temperature.

2.3. Determination of total phenolic content of extract

Phenolics contents of aqueous extract were estimated by the Folin-Ciocalteu colorimetric method [55]. In brief, 0.2 mL of the sample was mixed with 1 mL of a reagent Folin Ciocalteau 10% and allowed to stand for 4 minutes. After incubation, 0.8 mL of Na_2CO_3 (75 g/L) was added to mixture. After 30 minutes of standing at room temperature in dark, the absorbance was measured at 765 nm.

Phenolics contents are expressed as gallic acid equivalent per gram of powder (the equation regression was $y = 0,0052.x + 0,0258,\ r^2 = 0,9957$).

2.4. Determination of total flavonoids content of extract

Aluminum chloride colorimetric method was used to quantify flavonoids content [56]. 1 mL of each sample and standard (dissolved in ethanol) was added to 1 mL of $AlCl_3$ (2% in ethanol). The mixture was remained at room temperature for10 minutes in dark. Then, the absorbance was measured at 430 nm. This assay was realized in triplicate. Total flavonoids content were expressed as quercetin equivalent per gram of powder (the equation regression was $y = 0,0344.x + 0,0088,\ r^2 = 0,991$).

2.5. Determination of total flavonols content of extract

The assay is performed in a test tube. 2.8 mL of distilled water, 0.1 mL of $AlCl_3$, 0.1 mL of CH_3CO_2K (1 M), 0.5 mL of the extract are mixed, then incubated in the shade at room temperature for 30 minutes [57]. Absorbance was read at 415 nm. All determinations were carried out in triplicate. The flavonol content is expressed in milligrams quercetin equivalent per gram of powder (the equation regression was $y=0{,}008.x-0{,}016$, $r^2=0{,}998$).

2.6. *DPPH radical scavenging activity*

Radical scavenging activity (RSA) of T. algeriensis extract against the stable 1,1-diphenyl-2 -picryl hydrazyl radical (DPPH) was determined by a slightly modified DPPH free radical scavenging assay [58]. Briefly, 1.9 mL of a daily DPPH solution was added to 0.1 mL of aqueous extract (tested at concentrations ranging from 5 to 100 µg/mL). The absorbance of mixture was read after 30 of incubation. The scavenging activity DPPH radical was expressed as percentage inhibition by the following formula:

$$\left[\left(A_{blank}-A_{sample}\right)/A_{blank}\right]\times 100 \quad (1)$$

Where, A_{sample} is the absorbance of the solution containing the sample at 515 nm and A_{blank} is the absorbance of the DPPH solution. The IC_{50} values were calculated as the concentration of extract causing a 50% inhibition of DPPH radical.

2.7. Weight loss measurements

Gravimetric measurements were carried out at the definite time interval of 6 hours at constant temperatures (35, 40, 60, 70 °C and 80 ± 0.1 °C) using an analytical balance (precision ±0.1 mg). Specimens of rectangular shape (length = 1.6 cm, width = 1.6 cm, thickness = 0.07 cm) were immersed in 0.5 M of sulfuric acid containing different concentrations of inhibitors. After immersion period, the steel specimens were withdrawn, carefully rinsed with bidistilled water, ultrasonic cleaning in acetone, dried at room temperature and then weighted. Triplicate experiments were performed in each case and the mean value of the weight loss is calculated. The solution volume was 50 mL.

2.8. Polarization and EIS measurements

Potentiodynamic polarization experiments were conducted using a potentiostat PGZ100 piloted by Voltamaster soft-ware. A conventional three-electrode cylindrical Pyrex glass cell was used. The working electrode was carbon steel, platinum electrode as auxiliary electrode with surface area of 1 cm^2 and a saturated calomel electrode (SCE) was used as reference. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential (E_{ocp}) was obtained.

The polarization curves were plotted by polarization from -800 to -200 mV/SCE at 308 K with a scan rate of 1 mV/s. The EIS experiments were conducted in the frequency range of 100 kHz to 10 mHz, with 10 points per decade, by applying 10 mV ac voltage peak-to-peak. All impedance spectra were recorded at the steady state of open circuit potential, after 30 minutes of the exposure of the working electrode to the solution.

3. Results and discussion

3.1. T. algeriensis oil analysis

The analysis of essential oil from T. algeriensis was carried out by GC/MS. The chemical composition of essential oil was characterized by 10 compounds, which percentages are summarized in Table 1. The essential oil was characterized by high amounts of Geranyl acetate 7 (80.8%). The other major components were Geraniol 5 (7.3%) and trans-Caryophyllene 11 (2.4%). The 7 other compounds are reported in low amounts. It should be noted that numerous studies have been published on chemical composition of T. algeriensis. Among these studies, the study performed by Ait-Ouazzou et al. [59] during June 2009 in the north-eastern part of Morocco, in different areas of MergChoum, a mountain in Taourirt City, showed that borneol (23.48%) was the elevated individual compound in T. Algeriencis oil followed by linalool (8.99%), camphene (6.90%), carvacrol (7.76%), and β -caryophyllene (6.39%).

Based on the data obtained from our study and those of Ait-Ouazzou et al, it was noted that there is a considerable difference in the chemical composition of T. algeriensis oil. In fact this difference could be attributed to several factors such as the time of harvested, the period of sunshine, the nature and the composition of the ground [60].

Table 1: Chemical constituents of T. algeriensis oil (%)

Composés	IL	Ir /apol	Ir /pol	% apol
Limonene	1025	1023	1201	0.1
1,8-Cineole	1024	1023	1207	0.1
α-Terpineol	1176	1173	1671	0.2
Thymol methyl ester	1215	1220	1582	0.5
Geraniol	1235	1247	1833	7.3
Geranial	1244	1255	1714	0.6
Geranyl acetate	1362	1373	1750	80.0
α-Gurjunene	1413	1410	1524	0.6
trans-Caryophyllene	1421	1419	1561	2.4
Caryophyllene oxyde	1578	1569	1926	1.6
			TOTAL	98.1

3.2. Determination of total phenolic content (TPC), total flavonoids (TF) and flavonols

Generally, numerous reports have shown that radical scavenging activity (RAS) of plant extracts is coupled to phenolic compounds such as flavonoids and flavonols [61]. Thus, the total phenolic content, total flavonoids and flavonols of the plant extract were evaluated and listed in Table 2. This research and that reported by N khled Khoudja et al. [62], have shown that the content of polyphenols, flavonoids and flavonol of aqueous extract of T. algeriensis are quite similar.

Table 2: Phenolic compounds of aqueous extract of T. algeriensis

Extrait	TPC [(a)]	TF [(b)]	Flavonols[(b)]	Reference
TAE	117.50 ± 6.30	17.31 ±0.08	5.38 ± 0.08	Present study
TAE	99.21 ± 4.89	12.84 ±0.25	6.57 ±0.93	N. Khled khoudja et al. 2014

All the values are mean ± SD; SD: standard deviation

[(a)] (mg GAE/g powder).

[(b)] (mg QE/g powder).

3.3. Scavenging activity of DPPH radical

Several methods are available to investigate the antioxidant activities of compounds or complex mixtures, such as plant extracts. DPPH free radical has been used extensively due to its stability, ease and its simple reaction system which involves only the direct reaction between the radical and an antioxidant, which prevents further radical formation by donating hydrogen to highly reactive radical. For this purpose, radical scavenging activity (RSA) was studied spectrophotometrically by measuring the decrease in absorbance induced by plant antioxidants [63]. The results of extract aqueous and positive controls (ascorbic acid and BHA) are presented in Table 3.

Figure 1 shows that radical scavenging activity (RSA, %) increased with increasing amount of the extract and positive controls (ascorbic acid and BHA).

Table 3: DPPH radiacl scavenging activity of aqueous extract of T. algeriensis

Sample	Scavenging ability (%, Mean ± SD), concentration (µg/mL)						
	5.0	10.0	20.0	30.0	40.0	50.0	100.0
TAE	16.2 ± 1.7	23.0 ± 1.6	33.2 ± 1.0	47.7 ± 1.0	58.7 ± 1.0	72.3 ± 1.1	83.9 ± 1.1
BHA	51.0 ± 1.6	65.9 ± 1.5	83.1 ± 0.9	87.5 ± 0.1	88.5 ± 1.0	89.0 ± 1.2	89.7 ± 0.7
Ac. Asc	85.3 ± 1.3	93.0 ± 1.7	93.2 ± 1.2	93.4 ± 1.1	93.4 ± 1.5	93.8 ± 1.0	94.3 ± 1.0

All the values are mean ± SD; SD: standard deviation

From the IC_{50} value of aqueous extract (32.40 µg/mL) we noticed that this scavenging activity is lower than that exhibited from ascorbic acid (2.82 µg/mL) and that of BHA (5.55 µg/mL). Finally we can conclude that the aqueous extract of T. algeriensis exhibits a moderate antioxidant ability to reduce DPPH radicals.

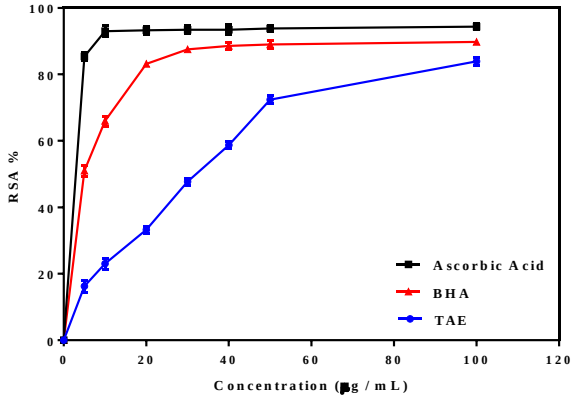

Figure 1: Radical Scavenging Activity of TAE

3.4. Gravimetric study

3.4.1. Effect of concentration

The effects of addition of TA inhibitors tested at different concentrations on 0.5 M H_2SO_4 solution were investigated by weight loss method at 308 K after 2 hours of immersion period. The inhibition efficiency (E_w%) was determined according to the following equation:

$$E_w\,\% = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \qquad (2)$$

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

Table 4 summarizes the gravimetric trends of the carbon steel immersed in 0.5 M H_2SO_4 in the absence and the presence of the inhibitors at various concentrations.

Table 4: Gravimetric results of mild steel in acid solutions 0.5 M H_2SO_4 at different concentration of TAE & TAO (308 K & 6 h).

Compounds	Concentrations (g/L)	W ($mg.cm^{-2}.h^{-1}$)	E_w %
Blank	1M	0.520	-
Thymus algeriensis Oil	0.25	0.152	70.7
	0.5	0.145	72.1
	1	0.107	79.4
	2	0.092	82.3
Thymus algeriensis Extract	0.25	0.067	87.0
	0.5	0.046	91.1
	1	0.035	93.2
	2	0.026	95.0

From the date listed in the table. 3, we can remark that the inhibition efficiency (E_w%) increases to reach 82.3 % and 95.0% for TAO and TAE at 2g/L, respectively, and the corrosion rate decreases with the increase of concentration of the tested inhibitors. Lastly, we can conclude that the net decrease in weight in the presence of TAE and TAO is an important sign that these compounds under investigation are efficient inhibitors of mild steel in test solutions.

3.4.2. Polarization curves

Polarization measurements are commonly accepted to provide the relevant information about the kinetics of electrochemical corrosion parameters. Typical potentiodynamic polarisation curves of mild steel in 0.5 M H_2SO_4 solutions in the presence and the absence of various concentrations of the tested inhibitors are shown in Figure 2.

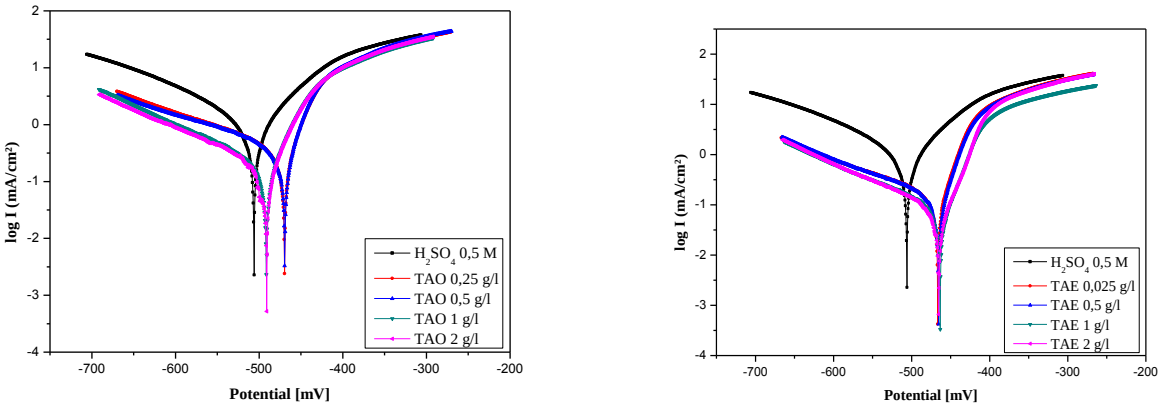

Figure 2: Cathodic and Anodic polarisation curves of mild steel in 0.5 M H_2SO_4 in the presence of T. algeriensis oil and extract at different concentrations.

Electrochemical parameters including corrosion current densities (I_{corr}), potential (E_{corr}), cathodic and anodic Tafel slopes (β_c, β_a) and inhibition efficiency (E_I %) determined from these experiments by extrapolation method [64], are reported in Table 5.

Table 5: Electrochemical parameters of steel at various concentrations of TAE and TAO respectively in 0.5 M H_2SO_4 and the corresponding inhibition efficiencies.

Inhibitors	Concentrations (g/l)	$-E_{corr}$ (mV)/SCE	$-\beta_c$ (mV/dc)	I_{corr} (µA/cm^2)	E_I %
blank	0.5 M	506	194.0	901.7	-
TAO	0.25	469	179.4	296.4	67.1
	0.5	469	183.6	269.3	70.1
	1	491	149.4	190.4	78.8
	2	490	147.0	146.3	83.7
TAE	0.25	466	150.5	100.1	88.9
	0.5	465	142.8	88.7	90.1
	1	463	138.4	65.5	92.7
	2	464	131.5	58.2	93.5

The I_{corr} values were used to calculate the inhibition efficiency E_I (%), (listed in Table 5), using the following equation [65]:

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

where I_{corr} and I'_{corr} are, respectively the uninhibited and inhibited current density. The corrosion current density was calculated from the intersection of cathodic and anodic Tafel lines.

From electrochemical parameter values listed in Table 5 it can be noted that I_{corr} values were progressively reduced in the presence of inhibitors with steady increase in the concentration from 901,7 to 146.3 and 58.2 µA/cm^2 with the highest concentration of TAO and TAE (2 g/L). The obtained efficiencies (E_l %) in the present work indicate that T. algeriensis inhibitors act as an effective inhibitors. The values of E_l (%) increase with the inhibitors concentration to reach 83.7% and 93.5% for TAO and TAE, respectively at 2 g/L. Our results were authentic and are confirmed by the previous works of Hamdani et al. (2015) who also worked on the oil and aqueous extract of T. algeriensis harvested from Sidi Maafa area, in Oujda Eastern Morocco [66,67].

Furthermore, the addition of T. algeriensis inhibitors to the aggressive media inhibited both cathodic and anodic reactions and this inhibition is more pronounced with increasing inhibitors concentrations. These results reveal that the addition of inhibitors reduced the anodic dissolution of mild steel and also retarded the hydrogen evolution reaction. The presence of inhibitors does not prominently shift the corrosion potential, which indicates the studied inhibitors (TAO & TAE) acts as mixed-type inhibitor [68]. Moreover, in the presence of these inhibitors, the slight change of β_c indicates that the cathodic corrosion mechanism of steel does not change.

3.5. Electrochemical impedance spectroscopy measurements

The electrochemical impedance spectroscopy (EIS) is a good technique to investigate the corrosion inhibition processes. It provides information on both the resistive and capacitive behavior at interface and makes it possible to evaluate the performance of the tested compounds as possible inhibitors against metals dissolution. The typical set of impedance diagrams of mild steel in uninhibited and inhibited acid solutions containing different concentrations of TAO and TAE are shown in Figure 3.

The EIS data has also been used for the exploration of inhibition performance of TA inhibitors. The curve shown in Figure 3 indicates a similar type of Nyquist plot for mild steel in the presence of various concentrations of TAO and TAE. As shown in Figure 3, the capacitive loops are slightly depressed as semi-circular shapes because of the roughness and other inhomogeneities of mild steel surface resulting in a phenomenon called ‘‘dispersing effect’’ [69, 70].

It is evident that the impedance response of mild steel has notably changed after the addition of TAO and TAE. The diameters of those loops increase with increasing concentrations of TAO and TAE. Our results are comparable to previous results of A. Khadraoui et al. who reported that the R_t values of the Algerian T. algeriensis were increased with increasing concentration for 2024 aluminium alloy in 1 M HCl medium [71].

The EIS data shows that the diameter of each Nyquist Plot semicircle gradually increases when the concentration was increased from 0.25 to 2 g/L. This increase of the diameters has clearly shown that the R_t values were also increased from 17 to 79.49 and 176.9 Ohms.cm^2 for TAO and TAE, respectively. The single semicircle indicates that charge transfer takes place at electrode/electrolyte interface, and the corrosion reaction of steel is controlled by the transfer process [72].

Table 5 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 [73], 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:

$$C_{dl} = \frac{1}{2\pi . f_m . R_t} \qquad (4)$$

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

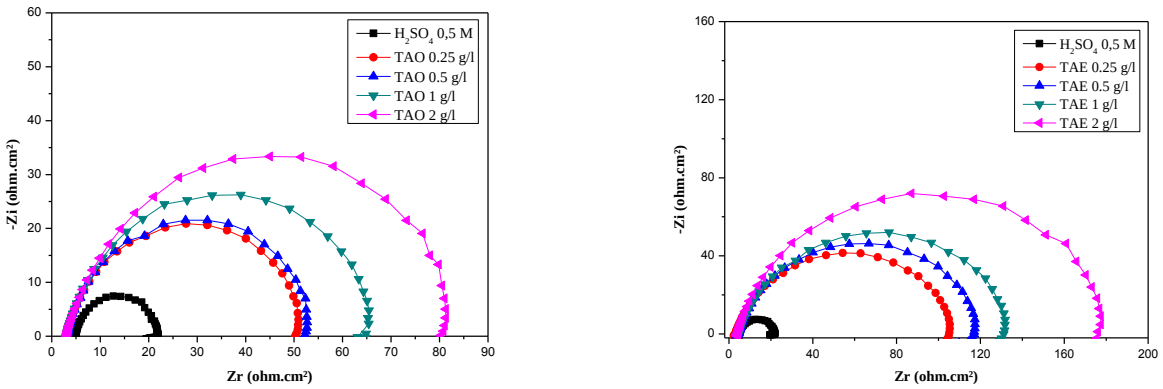

Figure 3: Nyquist diagrams for steel electrode with and without T. algeriensis inhibitors.

It is obvious from the data listed in table 6 that the values of inhibition’s efficiency increases with inhibitors concentrations to reach a maximum value 76.1 % and 91.**7** % at 2g/L for TAO and TAE, respectively.

The values of E_R% were calculated by the equation as follows:

$$E_R\% = \frac{R'_t - R_t}{R'_t} \times 100 \quad (5)$$

Table 6: Impedance parameters for corrosion of steel in acid at various contents of TAO and TAE respectively.

Inhibitors	Concentrations (g/L)	R_t (Ohm.cm^2)	f_{max} (Hz)	C_{dl} (µF.cm^{-2})	E_R %
Blank	1M	17	-	-	-
TAO	0.25	48.67	31.64	118.1	65.0
	0.5	50.19	25	138.5	66.1
	1	63.87	25	140.6	73.3
	2	79.49	25	130.8	76.1
TAE	0.25	103.9	20	76.6	85.8
	0.5	114.5	20	158.6	87.2
	1	129.6	15.82	86.5	88.7
	2	176.9	15.82	55.3	91.7

3.6. Effect of temperature

The effect of temperature on the inhibition reaction is highly complex. In fact, the temperature can modify the interaction between the mild steel and the acid medium such as rupture, desorption of inhibitor and the decomposition and/or rearrangement of inhibitor [74].

In order to study the effect of temperature on the corrosion inhibition property of TA inhibitors, gravimetric experiments were conducted in the range of 313–343 K temperature range during 1 h of immersion. The corresponding results are given in Table 7.

Table 7: Inhibition efficiency obtained from the corrosion rate at 2g/L of different inhibitors in 0.5 M H_2SO_4 at different temperatures at 1h immersion period.

T(K)	Blank W	TAE W	TAE E%	TAO W	TAO E%
313	0.89	0.40	64.4	0.80	78.8
323	1.35	0.53	71.4	1.18	65.2
333	2.85	0.87	76.3	2.19	56.2
343	5.83	1.56	83.6	4.68	50.8

Inspection of Table 7 reveals that in the absence and the presence of different inhibitors the increase of corrosion rate is more pronounced with the rise of temperature. We note also that the inhibition efficiency decreases to reach a value of 50.8% at 343 K for TAO and increases to attain a value of 83.6% at 343 K for TAO at 1h immersion period. On the other hand, the slight change in inhibition efficiency with temperature can be justified by modification of the strength of adsorption processes at high temperature [75]. From this result, we can deduce that TAO and TAE are excellent inhibitors.

3.6.1. Kinetic-thermodynamic parameters

The kinetic model is a tool of crucial practical importance to understand the mechanism of corrosion inhibition for the inhibitors. The activation parameters for the corrosion process of mild steel in the absence and presence of different concentrations of T. algeriensis were calculated from Arrhenius Eq. (5) and transition state Eq. (6) in the temperature range from 313 to 343 K [76]:

$$LnW = LnA - \frac{E_a}{R.T} \quad (6)$$

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.

$$Ln\frac{W}{T} = \left[Ln\left(\frac{RT}{Nh}\right) + \left(\frac{\Delta S_a^o}{R}\right)\right] - \frac{\Delta H_a^o}{RT} \qquad (7)$$

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.

Arrhenius plots for the corrosion rate of mild steel are given in Figure 3. Values of apparent activation energy of corrosion E_a in the absence and the presence of various concentrations of TAE and TAO were determined from the slopes of lnW versus 1000/T plots and shown in Table 7. All the linear regression coefficients are close to 1, indicating that corrosion of mild steel in 0.5 M H_2SO_4 can be elucidated using the kinetic model.

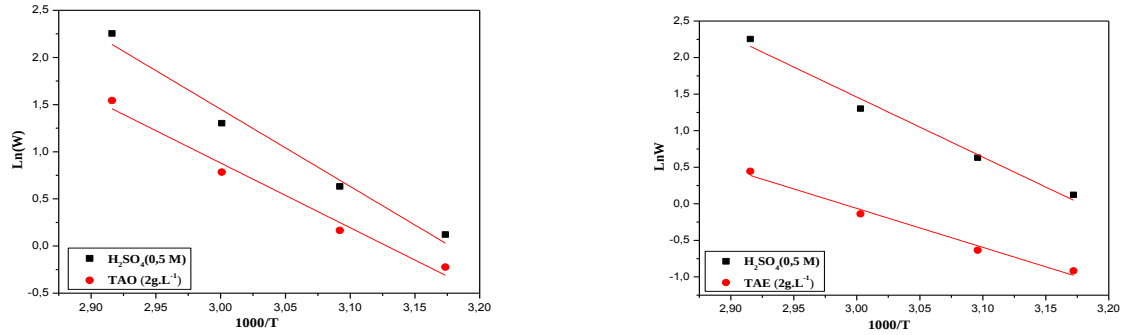

Figure 4: Arrhenius plots of mild steel for 2 g/L of TAE and TAO in 0.5 M H_2SO_4.

Table 8: Activation parameters for steel in 0.5 M H_2SO_4 in the absence and presence of TAE and TAO.

Inhibitors	ΔH_a $k\ j.mol^{-1}$	ΔS_a $j.K^{-1}.mol^{-1}$	E_a
Blank	65.3	-38.37	68.23
TAE	54.10	-76.18	44.28
TAO	41.34	-122.31	57.04

It is obvious from data given in Table 8 that the calculated values of activation energies decrease in the presence of inhibitors. Furthermore, the lower value of E_a of the corrosion process in an inhibitor's presence when compared to that in its absence is attributed to its chemisorption [77].

The relationship between Ln(W/T) and 1000/T is shown in Figure 4. Straight lines are obtained with a slope of ($-\Delta H_a / R$) and an intercept of (($\mathrm{Ln\,R/Nh} + \Delta S_a / R$)) from which the values of ΔH_a and ΔS_a are calculated and are given in Table 8. Analyses of these data reveals that the ΔH_a values for dissolution reaction of mild steel are lower in the presence of T. algeriensis inhibitors (54.10– 41.34 kJ.mol^{-1}) than that in its absence (65.30 kJ.mol^{-1}).

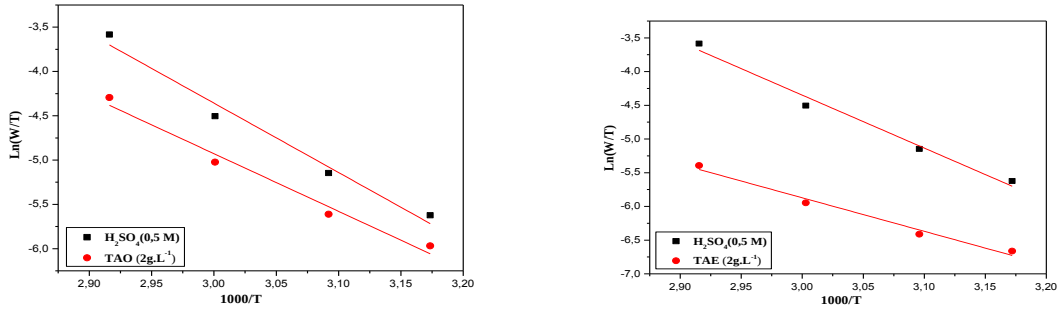

Figure 5: The variation of Ln (W/T) ~ f (1000/T) of the steel in 0.5 M H_2SO_4 with and without TAE and TAO.

The positive sign of ΔH_a show that the corrosion process of mild steel is an endothermic phenomenon signifying that its dissolution is slow in the presence of TAE and TAE [78]. The negative values of ΔS_a show 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 [79].

3.6.2. Adsorption isotherm

The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor has become very useful to give important clues to the nature of the metal–inhibitor interaction. In order to obtain the adsorption isotherm, The values of surface coverage θ for various concentrations of the inhibitors studied have been calculated at 303 K from the weight loss measurements by the ratio $E_W(\%)/100$. The most frequently used isotherms include: Langmuir, Frumkin, Temkin, Freundluich, Flory–Huggins, Dhar–Flory–Huggins, Bockris–Swinkels:

Temkin isotherm

$$\exp(f,\theta) = k_{ads}.C \quad (8)$$

Langmuir isotherm

$$\frac{\theta}{1-\theta} = k_{ads}.C \quad (9)$$

Frumkin isotherm

$$\frac{\theta}{1-\theta}\cdot\exp(-2f\cdot\theta) = k_{ads}\cdot C \quad (10)$$

Freundluich isotherm

$$\theta = k_{ads}\cdot C \quad (11)$$

With $K = \frac{1}{55.5}.\exp\left(-\frac{\Delta G_{ads}}{R.T}\right)$ (12)

Where C is the inhibitor bulk concentration in g/L, θ the fraction of the surface covered determined by E%/100 from weight loss measurements, 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. Figure 5 show the dependence of the ratio C/θ as function of C for TAE and TAO respectively.

In order to gain information about adsorption isotherm obeyed by inhibitors studied, a graphic relation between the inhibitor concentration C_{inh} and C_{inh}/θ, is drawn and represented in Figure 5. Straight line with almost unit slope and correlation coefficient ($0.99775 \le R \le 0.99423$) were obtained indicating that the system model follows Langmuir adsorption isotherm (Eq. (9)).

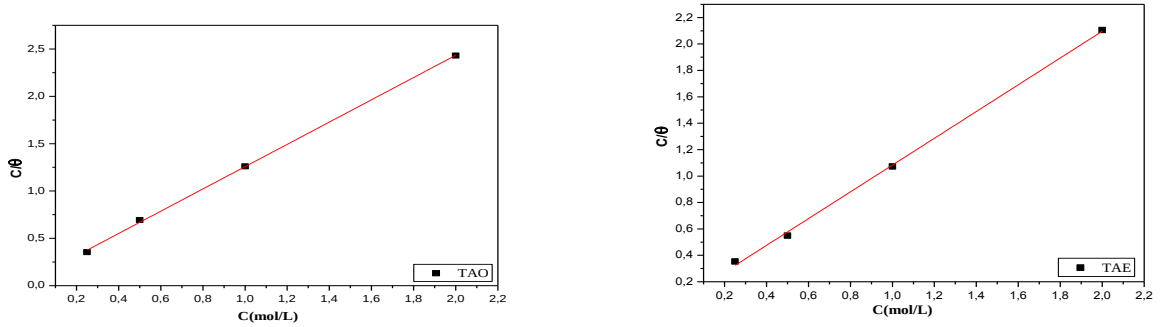

Figure 6: Plots of Langmuir adsorption isotherm of TAE and TAO on the steel surface at 308 K.

Conclusion

T. algeriensis (TA) was evaluated as a green effective corrosion inhibitor of mild steel in 0.5 M H_2SO_4 *solution by weight loss measurement, EIS and current–potential measurements. The results obtained* lead to the following conclusions:

- The GC/MS analysis of essential oil isolated from T. algeriensis (TA) plant shows that its composition is dominated by Geranyl acetate, Geraniol, trans-Caryophyllene and Caryophyllene oxyde (80.8%, 7.3%, 2.4% and 1.6%, respectively).

- Results of the antioxidant activity performed by DPPH have shown that the aqueous extract possess a moderate reducing power by comparing with the positive controls. Those results can be attributed to the existence of polyphenols compounds in the aqueous extract.
- The polarization studies showed that TAO and TAE inhibit both cathodic hydrogen reduction reactions and anodic metal dissolution, and then they act as mixed-type inhibitors of corrosion.
- The inhibition efficiency of TAE and TAO increases with the increase of inhibition concentration.
- The adsorption of the TA compounds on the mild steel surface in 0.5 M H_2SO_4 solution obeys Langmuir adsorption model.
- The values of inhibition efficiencies obtained from the different independent quantitative techniques used show the validity of the results.

T. algeriensis(TA) inhibitors 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.

References

1 Cronquist A., The New York Botanical Garden. New York, USA (1988).
2. Zaidi M. A., Crow S. A., J Ethnopharmacol. 96 (2005) 331.
3. Mabberley DJ., The plant-book. Cambridge: Cambridge University Press, (1997).
4. Maksimović Z., Stojanović D., Sostaric I., Dajić Z., Ristić M., *J. Sci. Food Agriculture*. 88 (2008) 2036.
5. Pellecuer J., Jacob M., Simeon de Buechberg M. & Allegrini J., *Acta Hortic*. 96 (1980) 35.
6. Benjilali B., Hammouni M., M'Hamedi A. & Richard H., *Sci. Aliments*. 7 (1987) 275.
7. Agnihotri S. & Vaidy A.D.B., *Indian J. Exp. Biol*. 34 (1996) 712.
8. Paster N., J. Juven B., Shaaya E., Menasherov M., Nitzan R., Weisslowicz H. and Ravid U., *Lett. Appl. Microbiol*. 11(1990) 33.
9. Caccioni D.R.L. & Guizardi D.R.L., *J. Essent. Oil Res*. 6 (1994) 173.
10. Cowan M.M., *Clin. Microbiol. Rev.*12 (1999) 564.
11. Nielsen P.V. & Rios R., *Int. J. Food Microbio.* 60 (2000) 219.
12. Lamiri A., Lhaloui S., Benjilali B. & Berrada M., *Field Crops Res.*71 (2001) 9.
13. Cimanga K., Kambu K. , Tona L., Apers S., De Bruyne T., Hermans N., Totté J., Pieters L., Vlietinck A.J, *J. Ethnopharmacology*. 79 (2002) 213.
14. Giweli A.A., Dzamic A.M., Sokovic M.D., Risti'c M.S., Marin, *Cent. Eur. J. Bot*. 7 (2013) 504.
15. Durnie W., De Marco R., Jefferson A., Kinsella B., *J. Electrochem. Soc*. 146 (1999) 1751.
16. Ellayyachy M., Elidrissi A., Hammouti B., *Corros. Sci*. 48 (2006) 2470.
17. Shukla S. K., Quraishi M.A., Prakash R., *Corros. Sci*. 50 (2008) 2867.
18. Zerfaoui, M., Oudda, H., Hammouti, B., Kertit, S., Benkaddour, M., *Prog. Org. Coat*. 51 (2004) 134-138.
19. Durnie W., De Marco R., Jefferson A., Kinsella B., *J. Electrochem. Soc*.146 (1999) 1751.
20. ElBelghiti M., Karzazi Y., Dafali A., Hammouti B., Bentiss F., Obot I.B., Bahadur I., Ebenso E.E., *J. Mol. Liq.* 218 (2016) 281.
21. ElBelghiti M., Karzazi Y., Dafali A., Obot I.B., Ebenso E.E., Emran K.M., Bahadur I., Hammouti B., Bentiss F., *J. Mol. Liq.*216 (2016) 874.
22. Yadav M., Sarkar T. K., Purkait T., *J. Mol. Liq*. 212 (2015) 731.
23. Ghazoui A., Zarrouk A., Bencaht N., Salghi R., Assouag M., El Hezzat M., Guenbour A., Hammouti B., J. *Chem. Pharm. Res.* 6 (2014) 704.
24. Tawfik S. M., Negm N. A., *J. Mol. Liq.* 215 (2016) 185.
25. Zarrok H., Oudda H., El Midaoui A., Zarrouk A., Hammouti B., Ebn Touhami M., Attayibat A., Radi S., Touzani R., *Res. Chem. Intermed.* 38 (2012) 2051.
26. Zarrok H., Zarrouk A., Salghi R., Oudda H., Hammouti B., Assouag M., Taleb M., Ebn Touhami M., Bouachrine M., Boukhris S., *J. Chem. Pharm. Res.* 4 (2012) 5056.
27. Herrag L., Hammouti B., Elkadiri S., Aouniti A., Jama C., Vezin H., Bentiss F., *Corros. Sci.* 52 (2010) 3042.
28. Singh P., Srivastava V., Quraishi M.A., *J. Mol. Liq.* 216 (2016) 164.
29. Ouchrif A., Zegmout M., Hammouti B., Dafali A., Benkaddour M., Ramdani A., Elkadiri S., *Prog.Org. Coat.* 53 (2005) 292.
30. Zarrok H., Zarrouk A., Salghi R., Assouag M., Hammouti B., Oudda H., Boukhris S., Al Deyab S.S., Warad I., *Der Pharm. Lett.* 5 (2013) 43.
31. Zarrouk A., Hammouti B., Zarrok H., Bouachrine M., Khaled K.F., Al-Deyab S.S., *Int. J. Electrochem. Sci.* 6 (2012) 89.
32. Zarrouk A., Hammouti B., Dafali A., Zarrok H., *Der Pharm. Chem.* 3 (4) (2011) 266.
33. Krishnegoweda P.M., Venkatesha V.T.M., Krishnegoweda P. K. M., Sivayogiraju S.B., *Ind. Eng. Chem. Res*. 52 (2013) 722.

34. Deng S., Li X., *Corros. Sci*. 55 (2012) 407.
35. Abiola O.K., James A.O., *Corros. Sci*. 52 (2010) 661.
36. El-Etre A.Y., *Corros. Sci*. 45 (2003) 2485.
37. Kamal C., Sethuraman M.G., *Ind. Eng. Chem. Res*. 51 (2012) 10399.
38. Ji G., Shukla S. K., Dwivedi P., Sundaram S., Prakash R., *Ind. Eng. Chem. Res*. 50 (2011) 11954.
39. Husnu G., Ibrahim S.H., *Ind. Eng. Chem. Res*. 51 (2012) 785.
40. Ji G., Dwivedi P., Sundaram S., Prakash R., *Ind. Eng. Chem. Res*. 52 (2013) 10673.
41. Gunasekaran G., Chauhan L.R., *Electrochimica Acta*. 49 (2004) 4387.
42. Umoren S. A., Gasem Z. M., Obot I. B., *Ind. Eng. Chem. Res*. 52 (2013) 14855.
43. Oguzie E.E., Oguzie K.L, Akalezi C.O., Udeze I. O., Ogbulie J.N., Njoku V.O., *ACS Sustainable Chem. Eng*. 1 (2013) 214.
44. Lecante A., Robert F., Blandinières P.A., Roos C., *Current Appl. Phys*. 11 (2011) 714.
45. Bammou L., Mihit M., Salghi R., Bouyanzer A., Al-Deyab S.S., Bazzi L., Hammouti B., *Int. J. Electrochem. Soc.* 6 (2011) 1454-1467.
46. De Assuncao Araujo Pereira S.S., Pegas M.M., Fernandez T.L., Magalhaes M., Schontag T.G., Lago D.C., De Senna L.F. and Elia E.D., Corros. Sci. 65 (2012) 360.
47. Abdel-Gaber A.M., Abd-El-Nabey B.A., Saadawy M., *Corros. Sci*. 51 (2009) 1038.
48. Bouyanzer A., Hammouti B., *Bull. Electrochem*. 20 (2004) 63-65.
49. Satapathy A.K., Gunasekaran G., Sahoo S.C., Kumar Amit, Rodrigues P.V., *Corros. Sci*. 51 (2009) 2848.
50. Chauhan L.R., Gunasekaran G., *Corros. Sci*. 49 (2007) 1143.
51. Saratha R., Kasthuri N., Thilagavathy P., *Der Pharm. Chem.* 1(2009) 249.
52. Abdel-Gaber A.M., Abd-El-Nabey B.A., Sidahmed I.M., El-Zayady A.M., Saadawy M., *Corros. Sci*. 48 (2006) 2765.
53. Nickavar B., Mojab F., Dolatbadi R., *Food Chem*. 90 (2005) 609.
54. Clevenger J. F, *J Am, Pharm Assoc*. 17 (1928) 346.
55. Wong C.C., Li H.B., Cheng K.W., *F. Chen, Food Chem*. 97 (2006) 705.
56. Djeridane A., Yous M., Nadjemi B., Boutassouna D., Stocker P., Vidal N., *Food Chem*. 97 (2006) 654.
57. Kosalec I., Bakmaz M., Pepeljnjak S, Vladimir-Knezević S., Acta Pharm. 54 (2004) 65.
58. Moure A., Franco D., Sineiro J., Domínguez H., Núnez M.J., Lema J.M., *J. Agric. Food Chem.* 48 (2000) 3890.
59. Ait-Ouazzou A., Loran S., Bakkali M., Laglaoui A., Rota C., Herrera A., Pagan R., Conchello P., *J Sci Food Agric*. 91 (2011) 2643.
60. Garneau F.X., Collin G.J., Huiles essentielles: de la plante à la commercialisation, le matériel végétal et les huiles essentielles, Chicoutimi, Quebec (2005) 1.
61. Chung K.T., Wong T.Y., Huang Y.W., Lin Y., *Rev. Food Sci. Nutr*. 38 (1998) 421.
62. Khled khoudja N., Boulekbache-Makhlouf L., Madani K., *Ind. Crop. Prod*. 52 (2014) 177.
63. Ksouri R., Falleh H., Megdiche W., Trabelsi N., Mhamdi B., Chaieb K., Bakrouf A., Magné C., Abdelly C., *Food Chem Toxicol*. 47 (2009) 2083.
64. Lebrini M., Bentiss F., Chihib N., Jama C., Hornez J.P., Lagrenée M., *Corros. Sci*. 50 (2008) 2914.
65. Bouklah M., Benchat N., Aouniti A., Hammouti B., Benkaddour M., Lagrenée M., Vezin H., Bentiss F., *Prog. Org. Coat*. 51 (2004) 118.
66. Hamdani I., El Ouariachi E., Mokhtari O., Salhi A., Chahboun N., ElMahi B., Bouyanzer A., Zarrouk A., Hammouti B and Costa J., *Der Pharm. Chem.*7 (2015) 252.
67. Hamdani I., El Ouariachi E., Mokhtari O., Salhi A., Bouyanzer A., Zarrouk A., Hammouti B and Costa J., *Der Pharma. Lett*. 7 (2015) 109.
68. Cao C., *Corros. Sci*. 38 (1996) 2073.
69. Ramesh S., Rajeswari S., *Electrochim. Acta*. 49 (2004) 811.
70. Achouri M.E., Ketit S., *Prog. Org. Coat*. 43 (2001) 267.
71. Khadraoui A., Khelifa A., Hachama K., Mehdaoui R., *J. Mol. Liq*. 214 (2016) 293.
72. Machnikova E., Whitmire K.H., Hackerman N., *Electrochim. Acta*. 53 (2008) 6024.
73. Oyama Y., Nishikata A., Tsuru T., *Journal of the Japan Institute of Metals*. 66 (2002) 690.
74. Sahu J. K., Sahu K. K., Ray A. K., *Journal of Materials-Design and Applications*. 226 (2012) 34.
75. Bouklah M., Attayibat A., Kertit S., Ramdani A., Hammouti B., *Appl. Surf. Sci*. 242 (2005) 399.
76. Herrag L., Hammouti B., Elkadiri S., Aouniti A., Jama C., Vezin H., Bentiss F., *Corros. Sci*. 52 (2010**)** 3042.
77. Ammar I. A., El Khorafi F. M, *Werkst. Korros*. 24 (1973) 702.
78. Guan N.M., Xueming L., Fei L., *Mater. Chem. Phys*. 86 (2004) 59.
79. Langmuir I., *J. Amer. Chem. Soc*. 39 (1947**)** 1848.