

Chemical Composition and Anti-Corrosive Activity of *Pulicaria Mauritanica* Essential Oil Against the Corrosion of Mild Steel in 0.5 M H₂SO₄

G. Cristofari¹, M. Znini², L. Majidi^{2,*}, A. Bouyanzer³, S.S. Al-Deyab⁴, J. Paolini¹, B. Hammouti³, J. Costa¹

¹ Université de Corse, UMR CNRS 6134, Laboratoire de Chimie des Produits Naturels, Faculté des Sciences et Techniques, Corse, France.

² Laboratoire des substances naturelles & synthèse et dynamique moléculaire, Faculté des Sciences et Techniques, Université My Ismail, Errachidia, Morocco.

³ LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, Oujda, Morocco.

⁴ Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

*E-mail: lmajidi@yahoo.fr

Received: 3 October 2011 / Accepted: 12 November 2011 / Published: 1 December 2011

Essential oil of aerial parts of *Pulicaria mauritanica* was obtained by hydrodistillation and analyzed by GC and GC/MS. This oil was tested as corrosion inhibitor of mild steel in 0.5M H₂SO₄ using weight loss measurements, electrochemical polarization and EIS methods. The analysis of *P. mauritanica* essential oil allowed the identification of 25 components, which accounted for 94.3% of the total oil which Carvotanacetone was the predominant compound constituting 87.3%. The inhibitory effect of this essential oil was estimated on the corrosion of mild steel in 0.5M H₂SO₄ using electrochemical polarisation and weight loss measurements. The corrosion rate of mild steel is decreased in the presence of essential oil. The inhibition efficiency was found to increase with oil concentration to attain 91.5% at 2g/L. Polarisation curves revealed that this oil act as mixed type inhibitor with a strong predominance of cathodic character. The temperature effect on the corrosion behaviour of mild steel in 0.5M H₂SO₄ without and with the inhibitor at 2 g/L was studied in the temperature range from 303 and 343 K. The adsorption of inhibitor onto the mild steel surface was found to be a spontaneous process and to follow the Langmuir adsorption isotherm. The associated activation energy has been determined.

Keywords: Corrosion inhibition, Hydrodistillation, Essential oil, *Pulicaria mauritanica*, Carvotancetone.

1. INTRODUCTION

Mild steel is extensively used in industry especially for structural applications, but its susceptibility to rusting in humid air and its high dissolution rate in acid media are the major obstacles for its use on larger scale [1]. As acidic media hydrochloric acid and sulphuric acid are generally used in industry for cleaning, decaling and pickling of steel structures, processes which are normally accompanied by considerable dissolution of the metal [2]. However, the aggressiveness of these acids in the solution against structural materials of mild steel, the use of inhibitors is one of the best methods of protecting metals against corrosion [3]. Most corrosion inhibitors are organic compounds having hetero atoms in their aromatic or long carbon chain. These organic compounds can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion rate.

Due to the toxicity of these corrosion inhibitors [3], there has been increasing search for green corrosion inhibitors which are environmentally friendly and are gotten from natural products such as plant extracts [4]. Recently, several studies have been carried out on the inhibition of corrosion of metals by plant extract especially essential oils. Thus, we previously reported that *Salvia aucheri* var. *mesatlantica* oil [5], *Mentha spicata* oil [6], *Mentha pulegium* oil [7], *Eucalyptus globulus* oil [8], *Simmondsia chinensis* oil [9], *Rosmarinus officinalis* oil [10-12], *Artemisia herba-alba* oil [13-15], *Lavendula dentata* oil [16], *Cedrus atlantica* oil [17] and *Foeniculum vulgare* oil [18] have been found to be very efficient corrosion inhibitors for mild steel in acid media. In this paper, our choice is focused to essential oil of *Pulicaria mauritanica* Coss.

P. mauritanica Coss., a species of the family *Asteraceae*, is an aromatic and endemic plant growing wild in South east of Morocco. It is an herb branched, woolly-rooted perennial and creeping; its leaves are less broad, oval-lanceolate, endowed with a very strong odour; the flowers are yellow where it blooms in March-May. The plant abounds woodlands, rockeries on dry rocky pastures and in the plains and low mountains up to 1500 m. This Moroccan medicinal plant locally known as "Ifanzi oudaden" is used for treatment various inflammations and also used as herbal tea and to make various delicious foods. To the best of our knowledge, the study of chemical composition of *Pulicaria mauritanica* is short. Indeed the oil is only described by Gattefosse and Igolen (1949) and gives the chief of constituent as carvotanacetone (81%).

The objective of this paper is to report for the first time the detailed chemical composition of essential oil from *Pulicaria mauritanica*. Also, the inhibitory effect of this oil on the corrosion of mild steel in 0.5 M H₂SO₄ has been evaluated using gravimetric and electrochemical polarization methods.

2. EXPERIMENTAL PART

2.1. Essential oil composition

2.1.1. Plant material

The aerial parts of *P. mauritanica* were harvested in March 2009 (full bloom) from Morocco at four locations: Errachidia (center), Mellab, Alnif and Zagora. Voucher specimens were deposited in the herbarium of the Faculty of Sciences and Technology at Errachidia (Morocco).

2.1.2. Essential oil isolation

The dried vegetal material (100 g) was water-distilled (3 h) using a Clevenger-type apparatus according to the method recommended in the European Pharmacopoeia [19], and the yield of the essential oil was approx 0.65%.

2.1.3. Oil fractionation

The aerial part essential oils of *P. mauritanica* (1 g) were chromatographed using an Automatized Flash Chromatography CFA system (Teledyne Isco, Inc. Lincoln, NE 68501-2531 USA) using normal phase silica (12 g, 15–40 μm , 60 \AA).

The apolar fraction (A) was eluted with hexane ($n\text{-C}_6\text{H}_{14}$) and the polar fractions (P) were eluted with a mixture of diisopropylether ($(i\text{Pr})_2\text{O}$)/hexane with increasing polarity. The elution gradient percentage of $(i\text{Pr})_2\text{O}/n\text{-C}_6\text{H}_{14}$ (time) was: 0% (3 min); 1.5% (5 min); 2.5% (15 min); 3% (5 min); 3.5% (7 min); 5% (5 min); 5–100% (7 min), and 100% (3 min). The oil fractionation led to one apolar fraction and 10 polar fractions.

2.1.4. GC analysis

GC analysis was carried out using a PerkinElmer Autosystem (Waltham, MA, USA) XL GC apparatus equipped with dual flame ionization detectors (FID) and fused-silica capillary columns (i.d. = 60 m \times 0.22 mm, film thickness = 0.25 μm) coated with polydimethylsiloxane (Rtx-1) and Rtx-wax (polyethyleneglycol).

The oven temperature was programmed from 60 to 230 $^\circ\text{C}$ at 2 $^\circ\text{C}/\text{min}$. and then held at 230 $^\circ\text{C}$ for 35 min. The injector and detector temperatures were maintained at 280 $^\circ\text{C}$. Samples were injected in the split mode (1/50) using helium as the carrier gas (1 ml/min). The injection volume of pure oil was 0.1 μl . The retention index (RI) of the compounds was determined relative to the retention time of a series of *n*-alkanes ($\text{C}_5\text{--}\text{C}_{30}$) using the Van den Dool and Kratz equations [20].

2.1.5. GC-EI/MS

Samples were analyzed using a PerkinElmer Turbo mass detector (quadrupole) coupled to a PerkinElmer Autosystem XL chromatograph equipped with Rtx-1 and Rtx-wax fused-silica capillary columns.

The carrier gas was helium (1 ml/min), the ion source temperature was 150 $^\circ\text{C}$. the oven temperature was programmed from 60 to 230 $^\circ\text{C}$ at 2 $^\circ\text{C}/\text{min}$. and then held at 230 $^\circ\text{C}$ for 35 min. The injector was operated in the split (1/80) mode at a temperature of 280 $^\circ\text{C}$. the injection volume was 0.2 μl of pure oil, the ionization energy was 70 eV, and the EI/MS data were acquired over the mass range 35–350 Da.

2.1.6. NMR analysis

All NMR spectra were recorded on a Bruker Avance (Wissembourg, France) 400 Fourier Transform spectrometer equipped with a 5 mm probe and operating at 100.13 MHz for ^{13}C -NMR. Compounds were dissolved in deuterated chloroform and all shifts referred to the internal standard tetramethylsilane (TMS). ^{13}C -NMR spectra were recorded with the following parameters: pulse with 4 μs (flip angle 45°); acquisition time 2.7 s for 128 K data with a spectral width of 25,000 Hz (250 ppm); CPD mode decoupling; digital resolution 0.183 Hz/pt. The number of accumulated scans was 5000 for each sample (containing ca. 40 mg of oil in 0.5 mL of deuteriochloroform) Exponential line broadening multiplication (1 Hz) of the free induction decay was applied prior to Fourier transformation. ^1H -NMR spectra were recorded with the following parameters: flip angle 30° ; acquisition time 2.56 s for 32 K data table with a spectral width of 7000 Hz (17.5 ppm).

2.1.7. Components identification

The identification of the components was based on:

(1) a comparison between the calculated retention indices on the polar (I_{rp}) and apolar (I_{ra}) columns with those of pure standard authentic compounds and literature data [21,22].

(2) a comparison of the mass spectra with those of our own library of authentic compounds and with those of a commercial library [22,23].

2.1.8. Quantification of essential oil constituents

Quantification of the essential oil components was carried out using the methodology reported by Bicchi et al. [24], and modified as follows. The response factor (RFs) of 29 standard compounds grouped into seven chemical groups (monoterpene hydrocarbons, sesquiterpene hydrocarbons, Alcohols, ketones, aldehydes, esters and others) was measured using GC [25]. RFs and calibration curves were determined by diluting each standard in hexane, at five concentrations, containing tridecane (final concentration = 0.7 g/100 g) as an internal standard. Analysis of each standard was performed in triplicate. For the quantification of the essential oil components, tridecane (0.2 g/100 g) was added as internal standard to the essential oil. The correction factor (average of the response factors from standards) of each chemical group was calculated and used to determine the essential oil component concentration (g/100 g) according to the chemical group.

2.2. Corrosion test

2.2.1. Weight loss measurements

The aggressive solution (0.5M H_2SO_4) was prepared by dilution of Analytical Grade 98% H_2SO_4 with double-distilled water. Prior to all measurements, the mild steel samples (0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron) were polished with different

emery paper up to 1200 grade, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and drying at room temperature.

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 mL with and without the addition of different concentrations of inhibitor ranging from 0.25 g/L to 2 g/L. The mild steel specimens used had a rectangular form (2 cm x 2 cm x 0.05 cm). The immersion time for the weight loss was 6 h at 298 K. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in $\text{mg}\cdot\text{cm}^{-2}\text{h}^{-1}$.

The corrosion rate (W) and inhibition efficiency E_w (%) were calculated according to the Eqs. (1) and (2) respectively:

$$W = \frac{\Delta m}{S \cdot t} \quad (1)$$

$$E_w \% = \frac{W_{\text{corr}} - W_{\text{corr(inh)}}}{W_{\text{corr}}} \times 100 \quad (2)$$

where Δm (mg) is the specimen weight before and after immersion in the tested solution, W_{corr} and $W_{\text{corr(inh)}}$ are the values of corrosion weight losses ($\text{mg}/\text{cm}^2\cdot\text{h}$) of mild steel in uninhibited and inhibited solutions, respectively, S is the area of the mild steel specimen (cm^2) and t is the exposure time (h).

2.2.2. Polarization and EIS measurements

Electrochemical measurements were carried out in a conventional three-electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) in the form of disc cut from steel has a geometric area of 1 cm^2 and is embedded in polytetrafluoroethylene (PTFE). A saturated calomel electrode (SCE) and a disc platinum electrode were used respectively as reference and auxiliary electrodes, respectively. The temperature was thermostatically controlled at $298 \pm 1\text{K}$. The WE was abraded with silicon carbide paper (grade P1200), degreased with AR grade ethanol and acetone, and rinsed with double-distilled water before use.

Running on an IBM compatible personal computer, the 352 Soft CorrTM III Software communicates with EG&G Instruments potentiostat–galvanostat model 263A at a scan rate of 0.5 mV/sec. Before recording the cathodic polarisation curves, the mild steel electrode is polarised at -800 mV for 10 min. For anodic curves, the potential of the electrode is swept from its corrosion potential after 30 min at free corrosion potential, to more positive values. The test solution is deaerated with pure nitrogen. Gas bubbling is maintained through the experiments.

In the case of polarization method the relation determines the inhibition efficiency (E_I %):

$$E_i \% = \frac{I_{\text{corr}} - I_{\text{corr (inh)}}}{I_{\text{corr}}} \times 100 \quad (3)$$

where I_{corr} and $I_{\text{corr (inh)}}$ are the corrosion current density values without and with the inhibitor, respectively, determined by extrapolation of cathodic and anodic Tafel lines to the corrosion potential.

The electrochemical impedance spectroscopy (EIS) measurements were carried out with the electrochemical system which included a digital potentiostat model Volta lab PGZ 100 computer at E_{corr} after immersion in solution without bubbling, the circular surface of mild steel exposing of 1 cm^2 to the solution were used as working electrode. 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 were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. The impedance diagrams are given in the Nyquist representation. Values of R_t and C_{dl} were obtained from Nyquist plots.

The charge-transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru and al. [26]. The inhibition efficiency got from the charge-transfer resistance is calculated by the following relation:

$$E_{R_t} \% = \frac{R'_t - R_t}{R'_t} \times 100 \quad (4)$$

R_t and R'_t are the charge-transfer resistance values without and with inhibitor respectively. R_t is the diameter of the loop.

The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{\text{max}}$) are found as represented in Eq. (5):

$$C_{dl} = \frac{1}{\omega \cdot R_t} \quad \text{where } \omega = 2 \pi \cdot f_{\text{max}} \quad (5)$$

Impedance diagrams are obtained for frequency range 100 KHz –10 mHz at the open circuit potential for mild steel in 0.5 M H_2SO_4 in the presence and absence of PM oil.

2.2.3. Effect of temperature

The effect of temperature on the inhibited acid–metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition [27]. The change of the corrosion rate at 2 g/L of the PM oil during 2 h of immersion with the temperature was studied in 0.5 M H_2SO_4 , both in the absence and presence of PM oil. For this purpose, gravimetric experiments were performed at different temperatures (308–353 K).

To calculate activation thermodynamic parameters of the corrosion process, Arrhenius Eq. (6) and transition state Eq. (7) were used [28]:

$$W = A \exp \left(\frac{-E_a}{RT} \right) \quad (6)$$

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^\ddagger}{R}\right) \exp\left(-\frac{\Delta H_a^\ddagger}{RT}\right) \quad (7)$$

where E_a is the apparent activation corrosion energy, R is the universal gas constant, A is the Arrhenius pre-exponential factor, h is the Plank's constant, N is the Avogrado's number, ΔS_a^\ddagger is the entropy of activation and ΔH_a^\ddagger is the enthalpy of activation.

3 RESULTS AND DISCUSSION

3.1. Essential oil composition

Table 1. Chemical composition of *P. mauritanica* essential oil from Morocco

N ^a	Components	RIa ^b	RIp ^c	Component concentration (g/100g) ^d		
				Four stations		
				Aerial parts		
				average ± SD	min	max
1	Isobutyl isobutyrate	900	1083	0.1 ± 0	0.13	0.13
2	α -Pinene	930	1021	0.1 ± 0	0.04	0.12
3	β -Pinene	971	1103	0.1 ± 0	0	0.05
4	<i>para</i> -Cymene	1012	1253	0.1 ± 0	0	0.1
5	1.8-Cineole	1021	1202	0.2 ± 0	0	0.19
6	Linalol	1084	1526	1.2 ± 0.7	0.36	2.10
7	Camphor	1121	1490	0.5 ± 0.1	0.38	0.58
8	(<i>Z</i>)-Verbenol	1129	1656	0.2 ± 0	0.15	0.25
9	Borneol	1150	1675	0.2 ± 0	0.00	0.20
10	Terpinen-4-ol	1162	1579	0.2 ± 0.1	0.13	0.36
11	<i>para</i> -Cymen-8-ol	1165	1818	0.6 ± 0.6	0.00	1.02
12	Decanal	1191	1478	0.2 ± 0.1	0.00	0.25
13	Carvotanacetone	1230	1656	87.3 ± 5.2	79.99	92.13
14	Carvenone	1233	1685	0.2 ± 0.1	0.00	0.23
15	Thymol	1272	2145	0.3 ± 0.1	0.26	0.39
16	Carvacrol	1281	2171	0.9 ± 0.8	0.41	2.05
17	Dihydroedulan	1284	1472	0.2 ± 0.2	0.07	0.43
18	2.5-Dimethoxycymene	1400	1835	0.7 ± 0.7	0.15	1.73
19	Geranyl acetone	1428	1826	0.1 ± 0	0.00	0.10
20	6-oxo-cyclonerolidol	1546	1954	0.5 ± 0.2	0.38	0.79
21	Caryophyllene oxide	1567	1945	0.6 ± 0.4	0.36	1.25
22	\square -Cadinol	1624	2133	0.1 ± 0.1	0.04	0.29
23	β -Eudesmol	1633	2236	0.2 ± 0.1	0.11	0.41
24	α -Cadinol	1637	2194	0.2 ± 0.1	0.05	0.30
25	(<i>E</i>)-Phytol	2098	2586	0.2 ± 0.2	0.00	0.34
Total				94.3 ± 4.0		
Monoterpene hydrocarbons				0.3		
Sesquiterpene hydrocarbons				0		
Oxygenated monoterpenes				91.8		
Oxygenated sesquiterpenes				1.9		
Other				1.1		

^a The numbering refers to elution order on apolar column (Rtx-1)

^b **RIa** = retention indices measured on the apolar column (Rtx-1)

^c **RIp** = retention indices measured on the polar column (Rtx-Wax)

^d Concentration of components (g/100 g) are calculated using Response Factors RFs according to their chemical group (see Table 1) and based on GC peak areas on the apolar column (Rtx-1)

The analysis of the *P. mauritanica* essential oil was carried out by GC, and GC–MS, using the methodologies described in the section 2. Twenty-four components of the essential oil were identified by comparing their electron ionization mass spectra and their retention indices with those of our own authentic compound library (Table 1). There were no data for carvotanacetone **13** in our own library. However, the occurrence of this compound was suggested by a comparison of the GC–MS data of a commercial library [23], and was confirmed by a comparison of the ^{13}C -NMR chemical shifts of this pure component in an oil fraction and those described in the literature [29].

The component concentrations (g/100 g of essential oil) were determined using correction factors for each chemical group (averages of the response factors of the standards), according to the methodology described in the section 2. The chemical compositions of four samples of *P. mauritanica* essential oil from Morocco were similar, both qualitatively and quantitatively. The mean values (\pm standard deviation) of each component concentration are given in Table 1. The chemical composition of the essential oil was strongly dominated by oxygenated monoterpenes (91.8%), especially carvotanacetone **13** ($87.3 \pm 5.2\%$). The other two most abundant compounds were linalool **6** ($1.2 \pm 0.7\%$) and carvacrol **16** ($0.9 \pm 0.8\%$). It should be noted that the oxygenated sesquiterpenes (1.9%) were represented only slightly in the essential oil and the sesquiterpene hydrocarbons were absent.

3.2 Corrosion tests

3.2.1. Weight loss measurements

The effect of addition of *P. mauritanica* essential oil (PM oil) tested at different concentrations on the corrosion of mild steel in 0.5M H_2SO_4 solution was studied by weight loss measurements at 298 K after 6 h of immersion period.

The values of percentage inhibition efficiency E_w (%) and corrosion rate (W) obtained from weight loss method at different concentrations of PM oil at 298 K are summarized in Table 2.

Table 2. Gravimetric results of mild steel in acid without and with addition of the PM oil at various contents ($t= 6\text{h}$, $T= 298\text{ K}$).

Inhibitor	Concentration	W (mg/h.cm ²)	E_w (%)
H_2SO_4	0.5 M	1.79	--
	0.25 g/L	0,38	78,8
	0.5 g/L	0,382	81,8
PM oil	1 g/L	0,248	86,5
	1.5 g/L	0,19	89,4
	2 g/L	0,15	91,5

It is clear that the PM oil inhibits the corrosion of mild steel in 0.5M H_2SO_4 solution, at all concentrations used in this study, and the corrosion rate (W) decreases continuously with increasing additive concentration at 298 K. Indeed, Fig. 1 shown that the corrosion rate values of mild steel

decrease when the inhibitor concentration increases while E_w (%) values of PM oil increase with the increase of the concentration reaching a maximum value of 91.5% at a concentration of 2 g /L. This behaviour can be attributed to the increase of the surface covered θ (E_w %/100), and that due to the adsorption of phytochemical components of the essential oil are adsorbed onto the mild steel surface resulting in the blocking of the reaction sites, and protection of the mild steel surface from the attack of the corrosion active ions in the acid medium. Consequently, we can conclude that the PM oil is a good corrosion inhibitor for mild steel in 0.5M H_2SO_4 solution.

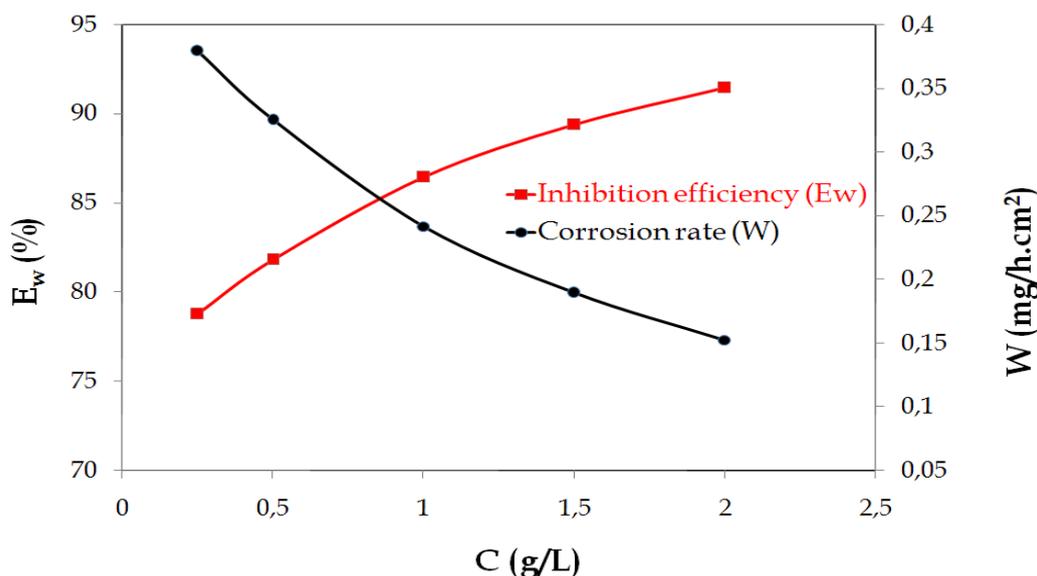


Figure 1. Variation of corrosion rate (W) and inhibition efficiency (E_w) of corrosion of mild steel in 0.5 M H_2SO_4 in the presence of PM oil.

In order to obtain a better understanding of the corrosion protection mechanism of PM oil against the corrosion of mild steel in normal sulphuric medium, a detailed study on this inhibitor was carried out using Tafel polarization and Electrochemical impedance spectroscopy (EIS) studies.

3.2.2. Polarization tests

Potentiodynamic anodic and cathodic polarization plots for mild steel specimens in 0.5M H_2SO_4 solution in the absence and presence of different concentrations of PM oil at 298 K are shown in Fig. 2. The respective kinetic parameters including corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c , β_a) and inhibition efficiency (IE%) are given in Table 3.

Inspection of Fig. 2 shows that the addition of PM oil has an inhibitive effect in the both anodic and cathodic parts of the polarization curves. Thus, addition of this inhibitor reduces the mild steel dissolution as well as retards the hydrogen evolution reaction. In addition, the parallel cathodic Tafel curves in Fig. 2 show that the hydrogen evolution is activation-controlled and the reduction mechanism

is not affected by the presence of the inhibitor [30]. As can be seen from the data of Table 3, the cathodic Tafel slopes β_c are approximately constant, indicating that the inhibiting action occurred by simple blocking of the available surface areas.

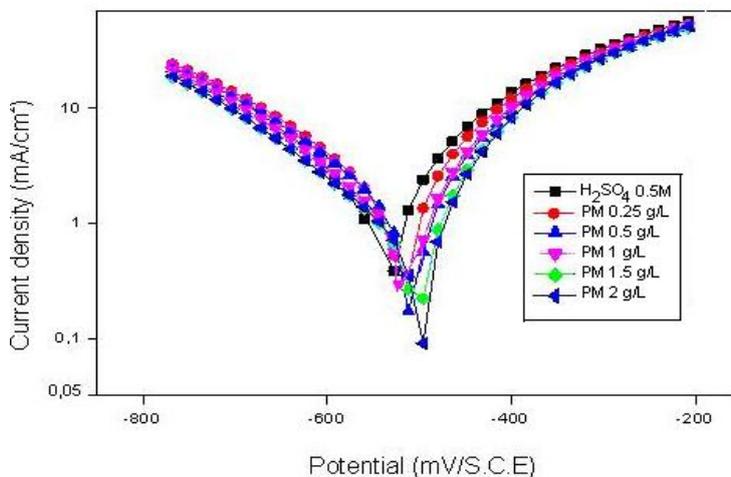


Figure 2. Polarization curves of mild steel in 0.5 M H₂SO₄ with and without PM oil at various concentrations at 298 K.

Table 3. Electrochemical parameters of mild steel at different concentrations of PM oil studied in 0.5 M H₂SO₄ at 298 K. Efficiencies corresponding corrosion inhibition.

Inhibitor	Concentration	-E _{corr} (mV)	I _{corr} (mA/cm ²)	β_a (mV)	$-\beta_c$ (mV)	IE%
H ₂ SO ₄	0.5 M	572.7	2.6564	194.1	235.6	-
	0.25 g/L	555.3	0.6043	190.4	234.6	74.9
	0.5 g/L	557.5	0.5492	174.4	225.8	79.8
PM oil	1 g/L	559.1	0.4472	173	234	81.7
	1.5 g/L	554.4	0.4441	148.7	187.9	82.2
	2 g/L	553.8	0.3487	142.7	181.1	86.1

In the domain anodic (Fig. 2), the polarization curves of mild steel have shown that the addition of the essential oil decreases the current density and moves the corrosion potential to positive values acting mainly on the dissolution reaction of metal. However, at potentials higher than -240 mV/sce, the presence of PM oil shows no effect on the anodic curves. This results suggest that the inhibitory action depends on the potential of inhibitor and a desorption process appears at high potential [31]. In this case, the desorption rate of the inhibitor is higher than its adsorption rate [32]. So, it could be concluded that this essential oil act as mixed type inhibitor with a strong predominance of cathodic character for mild steel in 0.5 M H₂SO₄ solution.

The analyse of the data in Table 3 revealed that the corrosion current density (i_{corr}) decreases considerably with increasing PM oil concentration, while no definite trend was observed in the shift of

E_{corr} values. The cathodic Tafel slope (β_c) show slight changes with the addition of PM oil, 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 natural oil concentration. The dependence of IE (%) versus the inhibitor concentration of PM oil is also presented in Table 3. The obtained efficiencies indicate that PM oil acts as a good corrosion inhibitor. Indeed, the values of IE (%) increase with inhibitor concentration, reaching its maximum value, 86.1%, at 2 g/L.

3.2.3. Electrochemical impedance spectroscopy (EIS)

The corrosion behaviour of mild steel in 0.5 M H_2SO_4 solution, in the absence and presence of PM oil, is also investigated by the electrochemical impedance spectroscopy (EIS) at 298K after 30 min of immersion.

Nyquist plots for steel in 0.5 M H_2SO_4 at various concentrations of this oil are presented in Fig 3.

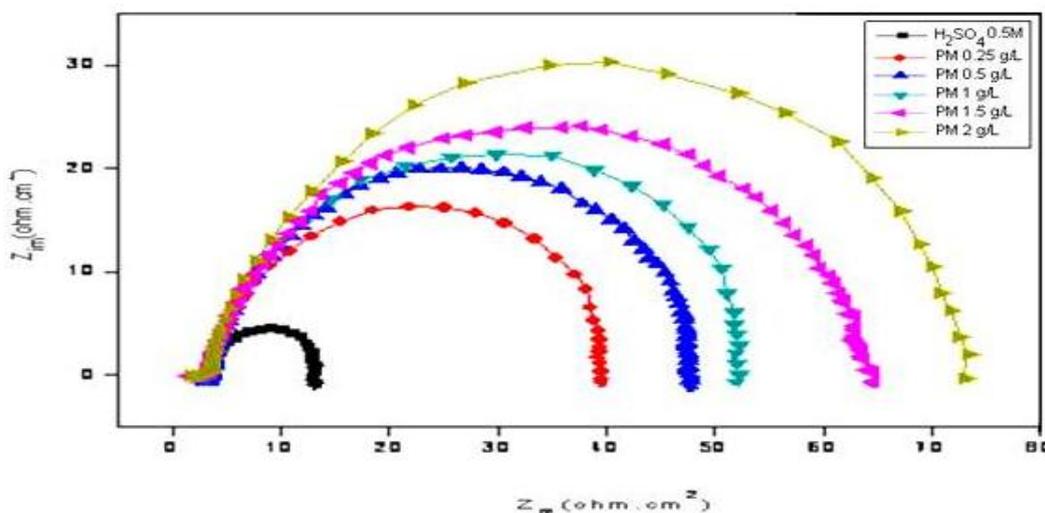


Figure 3. Nyquist plots of mild steel in 0.5 M H_2SO_4 containing various concentrations of PM oil

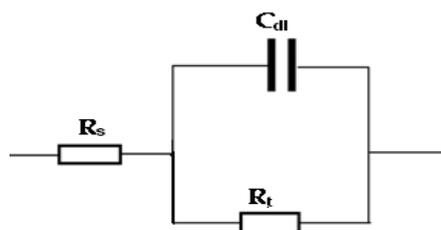


Figure 4. Equivalent circuit used to fit the EIS data of mild steel in 0.5 M H_2SO_4 without and with different concentrations of PM oil.

The EIS results are simulated by the equivalent circuit shown in Fig. 4 to pure electric models that could verify or rule out mechanistic models and enable the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system under investigation [33]. In the electrical equivalent circuit, R_s is the solution resistance, R_t the charge transfer resistance and C_{dl} is the double layer capacitance.

Table 4 gives values of charge transfer resistance, R_t double-layer capacitance, C_{dl} , and f_{max} derived from Nyquist plots and inhibition efficiency E_{Rt} (%).

Table 4. Characteristic parameters evaluated from the impedance diagram for mild steel in 0.5 M H_2SO_4 at various concentrations of PM oil.

Inhibitor	Concentration	$-E_{corr}$ (mV/SCE)	R_t ($\Omega.cm^2$)	f_{max} (Hz)	C_{dl} ($\mu F.cm^2$)	E_{Rt} %
H_2SO_4	0.5M	572	10.78	316.46	3096	--
	0.25 g/L	555	24.71	160	457	61.4
	0.5 g/L	557	28.77	155	436	63.7
PM oil	1 g/L	559	53.82	100	241	74.9
	1.5 g/L	554	54.13	78.291	125	80.0
	2 g/L	553	97.02	61.646	54	88.9

The recorded EIS spectrum for mild steel in 0.5 M H_2SO_4 at 298 (Fig. 3) showed one single depressed capacitive loop. The same trend (one capacitive loop) was also noticed for mild steel immersed in 0.5 M H_2SO_4 containing PM oil (0.25–2 g/L). The diameter of Nyquist plots increased on increasing the concentration of PM oil indicating strengthening of inhibitive film. Moreover, the single capacitive loop can be attributed to the charge transfer that takes place at electrode/solution interface, and the charge transfer process controls the corrosion reaction of mild steel and the presence of inhibitor does not change the mechanism of dissolution of mild steel [34]. It is also clear that these impedance diagrams are not perfect semicircles and this difference has been attributed to frequency dispersion [35], to roughness and other inhomogeneities of solid surface [36].

From the impedance data (Table 4), we conclude that the R_t values increase with inhibitor concentration and consequently the inhibition efficiency increases to 88.9% at 2 g /L. In fact, the presence of PM oil is accompanied by the increase of the value of R_t in acidic solution confirming a charge transfer process mainly controlling the corrosion of mild steel. 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} follows the order similar to that obtained for I_{corr} in this study. The decrease in C_{dl} is due to the adsorption of the inhibitor on the metal surface leading to the formation of film or complex from acidic solution [37]. We also note the increase of the value of R_t with the inhibitor concentration leading to an increase in the corrosion inhibition efficiency.

The variation of inhibition efficiency (E %), determined by the three methods (weight loss, polarization curves and EIS methods), as a function of concentration of PM oil in 0.5 M H_2SO_4 was

presented in Fig. 5. The results thus obtained show a good agreement with the three methods used in this investigation, significantly in high concentrations.

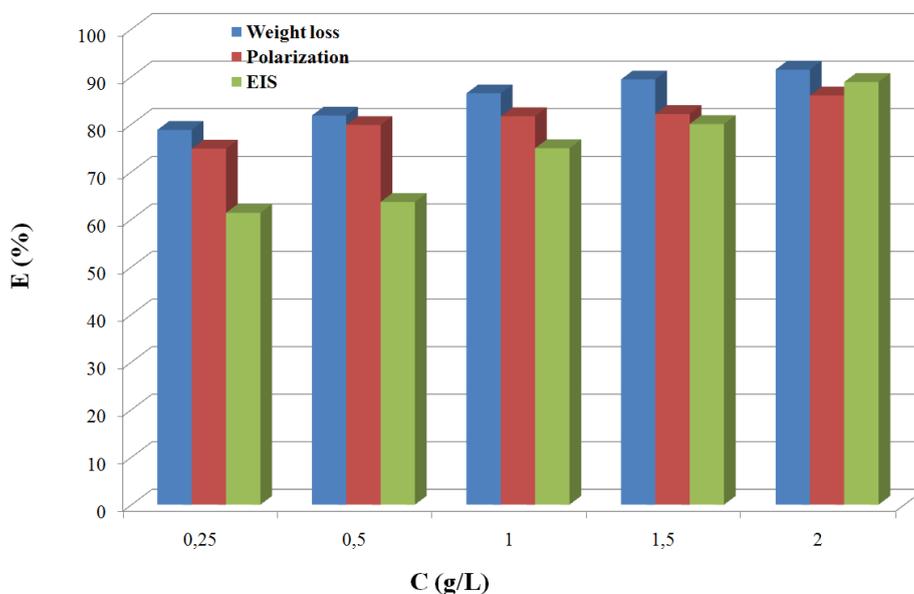


Figure 5. Comparison of inhibition efficiency (E%) values obtained by weight loss, polarization and EIS methods.

3.2.4. Effect of temperature

The data of corrosion rates and corresponding efficiency (Ew) collected were presented in Table 5.

Table 5. Corrosion parameters obtained from weight loss for mild steel in 0.5 M H₂SO₄ containing 2 g/L of PM oil at different temperatures.

T (K)	W (mg/h.cm ²)	W ₀ (mg/h.cm ²)	Ew (%)
303	0.217	1.764	87.7
313	0.491	4.211	88.3
323	0.661	7.125	90.7
333	1.127	14.00	91.9
343	1.670	21.78	92.3

Examination of this Table reveals corrosion rate increases both in the uninhibited and inhibited acid solution with the rise of temperature. The presence of inhibitor leads to decrease of the corrosion rate. Also, we note that the efficiency (Ew %) depends on the temperature and increases with the rise of temperature from 303 to 343 K. The increase in Ew% indicates that the inhibitory effect of oil is

reinforced at elevated temperature. The apparent activation energy (E_a) was determined from the slopes of $\ln(W)$ vs $1/T$ graph depicted in Fig. 6.

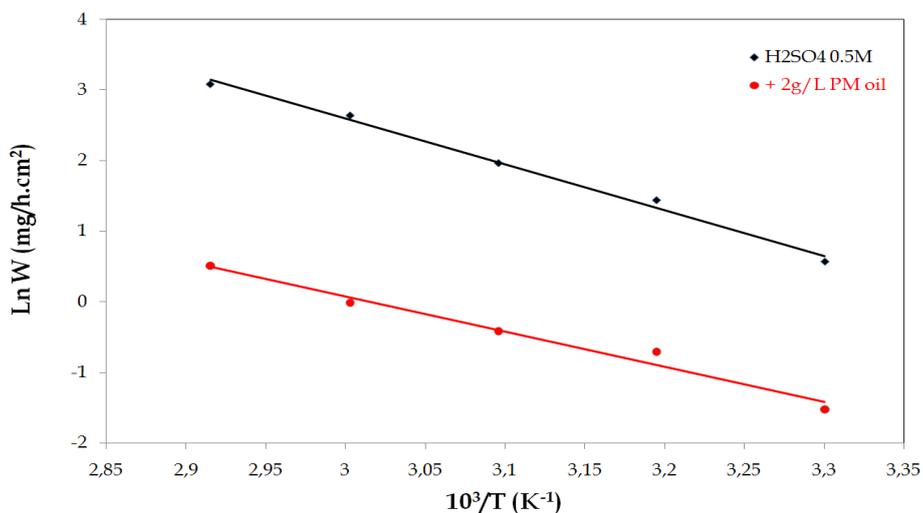


Figure 6. Arrhenius plots for mild steel corrosion rates (W) in 0.5 M H_2SO_4 in absence and in presence of 2 g/L of PM oil.

Values of apparent activation energy of corrosion (E_a) for mild steel in 0.5 M H_2SO_4 with the absence and presence of 2 g/L of PM oil were determined from the slope of $\ln(W)$ versus $1/T$ plots and shown in Table 6.

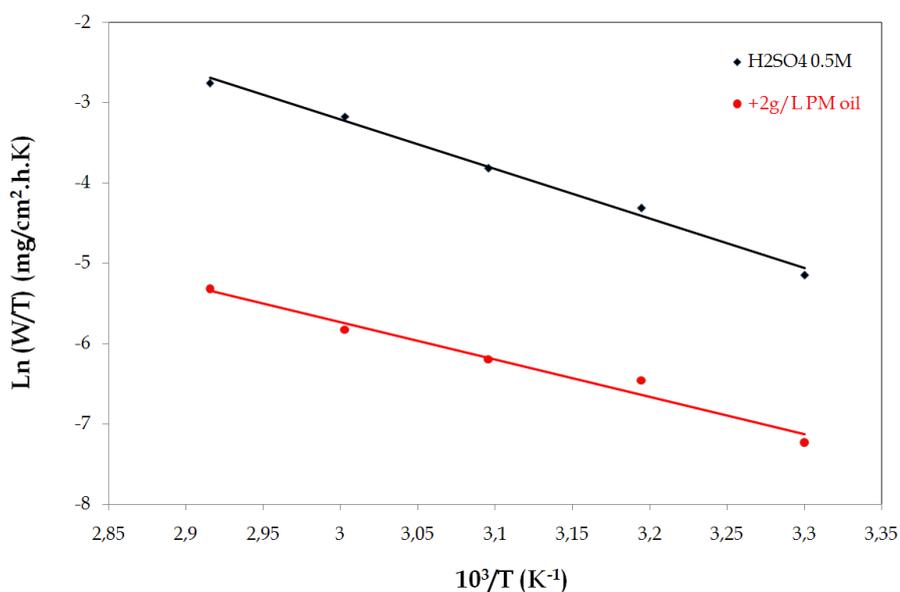


Figure 7. Transition-state plots for mild steel corrosion rates (W) in 0.5 M H_2SO_4 in absence and in presence of 2 g/L of PM oil.

Fig. 7 shows a plot of $\ln (W/T)$ against $1/T$. A straight lines are obtained with a slope of $(-\Delta H_a^\circ/R)$ and an intercept of $(\ln R/Nh + \Delta S_a^\circ/R)$ from which the values of ΔH_a° and ΔS_a° are calculated, are listed in Table 7.

Table 6. Corrosion kinetic parameters for mild steel in 0.5 M H_2SO_4 in the absence and presence of 2 g/L of PM oil.

Inhibitor	E_a (KJ. mol ⁻¹)	ΔH_a° (KJ. mol ⁻¹)	$E_a - \Delta H_a^\circ$ (KJ. mol ⁻¹)	ΔS_a° (J. mol ⁻¹ .K ⁻¹)
H_2SO_4 0.5M	54	51,13	2.87	-70.39
+2 g/L PM oil	42.54	39.85	2.69	-129.23

The calculated values of activation energies from the slopes are 54 and 42.54 kJ/mol for free acid and with the addition of 2 g/L of PM oil, respectively. We remark that the activation energy decreases in the presence of inhibitor. This results show that the addition of PM oil decreases metal dissolution in 0.5 M H_2SO_4 medium. Furthermore, the increase of $E_w\%$ is explained by Ammar and El Khorafi [38] as chemisorption of inhibitor molecules on the mild steel surface. 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 [39].

Moreover, inspection of the data of Table 6 reveals that the ΔH_a° values for dissolution reaction of mild steel in 0.5 M H_2SO_4 in the presence of 2 g/L of PM oil are lower (39.85 kJ mol⁻¹) than that of in the absence of inhibitor (51.13 kJ mol⁻¹). The positive signs of ΔH_a° reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow in the presence of inhibitor [40].

The average difference value of the $E_a - \Delta H_a$ is 2.69 kJ mol⁻¹, which is approximately equal to the average value of RT (2.69 kJ mol⁻¹) at the average temperature (323 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known of perfect gas [41].

On the other hand, the entropy of activation (ΔS_a°) in the absence and presence of essential oil has large and negative values. This indicates that the activated complex in the rate determining step represents an association rather than dissociation, meaning that a decrease in disordering takes place on going from reactants to the activated complex [42].

3.2.5. Adsorption isotherm

In order to acquire a better understanding of the adsorption mode of the inhibitor on the surface of the mild steel, the data obtained from the three different techniques were tested with several adsorption isotherms, including Langmuir, Frumkin, and Temkin. The Langmuir isotherm (C/θ vs C) assumes that there is no interaction between adsorbed molecules on the surface. The Frumkin

adsorption isotherm (θ vs C) assumes that there is some interaction between the adsorbates, and the Temkin adsorption isotherm (θ vs $\lg C$) represents the effect of multiple layer coverage [43].

The dependence of the fraction of the surface covered θ obtained by the ratio $E\%/100$ as function of the oil concentration (C_{inh}) was graphically fitted for various adsorption isotherms.

Fig. 8 shows that the relationship between C_{inh}/θ and C_{inh} , at 298 K, yields a straight line with correlation coefficient (R^2) was almost equal to unity (0.998) and the slopes was very close to unity (1.065). This behaviour suggests that the adsorption of PM oil on mild metal surface followed the Langmuir adsorption isotherm. This isotherm may be written in the following form:

$$\frac{C_{inh}}{\theta} = \frac{1}{b} + C_{inh} \quad (8)$$

C_{inh} is the inhibitor concentration; θ is the fraction of the surface covered, b is the adsorption coefficient.

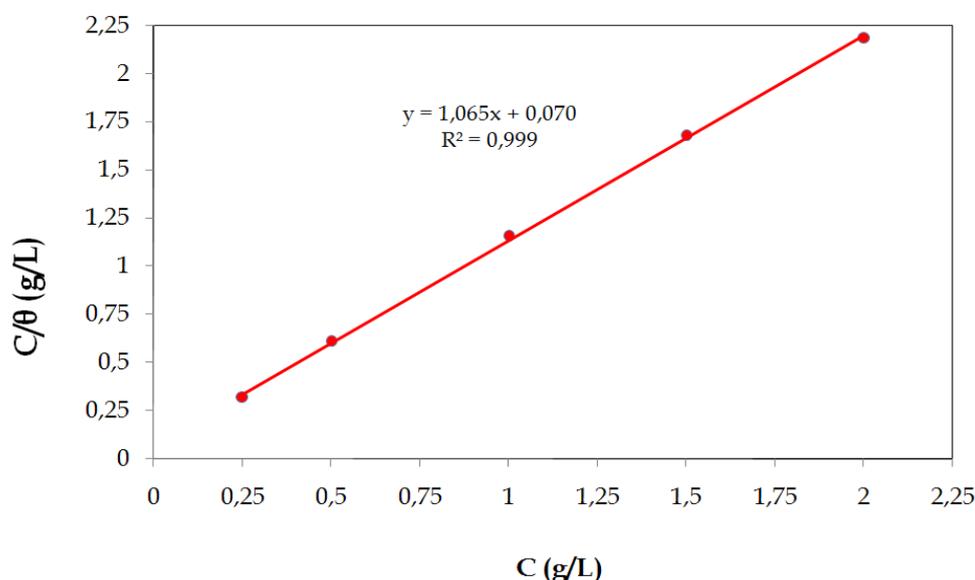


Figure 8. Langmuir adsorption isotherm of PM oil on the mild steel surface

3.2.6. Mechanism of inhibition of PM oil

The gravimetric method, polarisation curves and electrochemical impedance spectroscopy confirms the inhibiting character of PM oil in acid solution. However, the inhibition efficiency increases with essential oil concentrations. This result suggests that the probable mechanism can be explained on the basis of adsorption process and the structure of the constituents present in the essential oil. The inhibition may be due to the adsorption of phytochemical constituents present in the oil by one and/or more of the following two modes: In one mode, the neutral molecules may be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the oxygen atoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis

of donor–acceptor interactions between π -electrons of the aromatic ring and vacant d-orbitals of surface iron atoms. In second mode, since it is well known that the mild steel surface bears positive charge in acid solution [44], it is difficult for the protonated molecules to approach the positively charged mild steel surface (H_3O^+ /metal interface) due to the electrostatic repulsion. Since SO_4^{2-} have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, the protonated inhibitors adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus, there is a synergism between adsorbed SO_4^{2-} ions and protonated inhibitors. Thus, inhibition of mild steel corrosion in 0.5 M H_2SO_4 is due to the adsorption of phytochemical constituents on the mild steel surface [45,46].

Presumably, the adsorption of *P. mauritanica* essential oil is probably made by carvotanacetone which is the main component (87.3%). However, a synergistic or antagonistic effect of other molecules may play an important role on the inhibition efficiency of this oil.

4. CONCLUSION

The study of chemical composition and effect of *Pulicaria mauritanica* essential oil on the corrosion of mild steel in 0.5 M H_2SO_4 conducted by weight loss measurements and electrochemical method may draw the following conclusions:

- (1) Twenty-five compounds were identified for the first time in *P. mauritanica* essential oil, accounting for 94.3% of the total oil. Carvotanacetone strongly dominated the oil composition (87.3%);
- (2) Inhibition efficiency increases with both the concentration of inhibitor and temperature;
- (3) *Pulicaria mauritanica* oil acts as good inhibitor for the corrosion of mild steel in 0.5 M H_2SO_4 with an inhibition efficiency 91.5% at 2g/L;
- (4) The essential oil acts on mild steel surface in 0.5 M H_2SO_4 solution as mixed type inhibitor with a strong predominance of cathodic character;
- (5) Inhibition efficiency on mild steel may occur probably by action of carvotanacetone.

ACKNOWLEDGEMENTS

Prof S. S. Al-Deyab and Prof B. Hammouti extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group project.

References

1. S. Bilgic, N. Caliskan, *J. Appl. Electrochem.* 31 (2001) 79.
2. L.R. Chauhan, G. Gunasekaran, *Corros. Sci.* 49 (2007) 1143.
3. N.O. Eddy, E.E. Ebenso, *Afr. J. Pure Appl. Chem.* 2 (2008) 46.
4. G.O. Avwiri, F.O. Igbo, *Mater. Lett.* 7 (2003) 3705.

5. M. Znini, L. Majidi, A. Bouyanzer, J. Paolini, J.M. Desjobert, J. Costa, B. Hammouti, *Arab. J. Chem.* (2010), doi: 10.1016/j.arabjc.2010.09.017
6. M. Znini, M. Bouklah, L. Majidi, S. Kharchouf, A. Aouniti, A. Bouyanzer, B. Hammouti, J. Costa, S.S. Al-Deyab, *Int. J. Electrochem. Sci.*, 6 (2011) 691.
7. A. Bouyanzer, B. Hammouti, L. Majidi, *Material Letters*. 60 (2006) 2840.
8. A. Bouyanzer, L. Majidi, B. Hammouti, *Bull. Electrochem.* 22 (2006) 321.
9. A. Chetouani, B. Hammouti, M. Benkaddour, *Pigm. Resin. Technol.* 33 (2004) 26.
10. E. Chaieb, A. Bouyanzer, B. Hammouti, M. Benkaddour, M. Berrabah, *Trans. SAEST*. 39 (2004) 58.
11. M. Bendahou, M. Benabdellah, B. Hammouti, *Pigm. Resin. Technol.* 35 (2006) 95.
12. E. El-Ouariachi, J. Paolini, M. Bouklah, A. Elidriissi, A. Bouyanzer, B. Hammouti, J.M. Desjobert, J. Costa, *Acta Metall. Sin.* 23 (2010) 13.
13. A. Bouyanzer, B. Hammouti, *Pigm. Resin. Technol.* 33 (2004) 287.
14. M. Benabdellah, M. Benkaddour, B. Hammouti, M. Bendahou, A. Aouniti, *Appl. Surf. Sci.* 252 (2006) 6212.
15. O. Ouachikh, A. Bouyanzer, M. Bouklah, J-M. Desjobert, J. Costa. B. Hammouti, L. Majidi, *Surf. Rev. and Letters*. 16 (2009) 49.
16. B. Zerga, M. Sfaira, Z. Rais, M. Ebn Touhami, M. Taleb, B. Hammouti, B. Imelouane, A. Elbachiri, *Mater. Tech.* 97 (2009) 297.
17. A. Bouyanzer, L. Majidi, B. Hammouti, *Phys. Chem. News.* 37 (2007) 70.
18. N. Lahhit, A. Bouyanzer, J.M. Desjobert, B. Hammouti, R. Salghi, J. Costa, C. Jama, F. Bentiss, F. L. Majidi, *Portug. Electrochim. Acta* 29 (2011) 127.
19. European Pharmacopoeia, "Council of Europe". Strasbourg, 3rd ed, (1997) 121.
20. H. Dool, P. Kratz, *J. Chromatogr.* 11 (1963) 463.
21. D. Joulain, König, W.A., The atlas of spectral data of sesquiterpene hydrocarbons. EbVerlag Hamburg. (1998).
22. D. Hochmuth, D. Joulain, König, W.A., Terpenoids and related constituents of essential oils, Library of Massfinder 2. 1 University of Hamburg Institute of organic chemistry Hamburg Germany. (2001).
23. R.P. Adams, Identification of Essential Oil Components by Gas Chromatography/Quadrupole Mass Spectroscopy. Allured Publishing: Carol Stream. 2004.
24. C. Bicchì, E. Liberto, M. Matteodo, B. Sgorbini, L. Mondello, B.A. Zellner, R. Costa et al., *Flav. Frag. J.* 23 (2008) 382.
25. J. Paolini, T. Barboni, J-M. Desjobert, N. Djabou, A. Muselli, J. Costa, *Biochem. Syst. Ecol.* 38 (2010) 865.
26. S.H. Tsuru, B. Gijutsu, *J. Jpn. Soc. Corros. Eng.* 27 (1978) 573.
27. F. Bentiss, M. Lebrini, M. Lagrenée, *Corros. Sci.* 47 (2005) 2915.
28. J.O.M. Bockris, B. Young, *J. Electrochem. Soc.* 138 (1999) 2237.
29. S.A. Ross, K.A. El Sayed, M.A. El Sohly, M.T. Hamann, O.B. Abdel-Halim, A.F. Ahmed, M.M. Ahmed. *Planta. med.* 63 (1997) 479.
30. M. Bouklah, N. Benchat, A. Aouniti, B. Hammouti, M. Benkaddour, M. Lagrenée, H. Vezine, F. Bentiss, *Prog. Org. Coat.* 51 (2004) 118.
31. F. Bentiss, M. Traisnel, N. Chaibi, B. Mernari, H. Vezin, M. Lagrenée, *Corros. Sci.* 44 (2002) 2271.
32. M. Benabdellah, A., Aouniti, A., Dafali, B., Hammouti, M., Benkaddour, A., Yahyi, A., Ettouhami, *Appl. Surf. Sci.* 252 (2006) 8341.
33. A.R.S. Priya, V.S. Muralidharam, A. Subramanian, *Corrosion*, 64 (2008) 541.
34. Y. Larabi, M. Harek, M. Traisnel, A. Mansri, *J. Appl. Electrochem.* 34 (2004) 833.
35. F. Mansfeld, M.W. Kending, S. Tsai, *Corrosion*. 38 (1982) 570.
36. K. Juttner, *Electrochim. Acta.* 35 (1990) 1501.

37. M. Lagrenée, B. Mernari, M. Bouanis, M. Traisnel, F. Bentiss, *Corros. Sci.* 44 (2002) 573.
38. I.A. Ammar, F. M. El Khorafi, *Werkst. Korros.* 24 (1973) 702.
39. A. Zarrouk, B. Hammouti, R. Touzani, S.S. Al-Deyab, M. Zertoubi, A. Dafali, S. Elkadiri, *Int. J. Electrochem. Sci.*, 6 (2011) 939-4952.
40. N.M. Guan, L. Xueming, L. Fei, *Mater. Chem. Phys.* 86 (2004) 59.
41. M.K. Gomma, M.H. Wahdan, *Mater. Chem. Phys.* 39 (1995) 209.
42. S. Samkarapapaavinasam, M.F. Ahmed, *J. Appl. Electrochem.* 22 (1992) 390.
43. N. Labjar, M. Lebrini, F. Bentiss, N. Chihib, S. El Hajjaji, C. Jama, *Mater. Chem. Phys.* 119 (2010) 330.
44. G.N. Mu, T.P. Zhao, M. Liu, T. Gu, *Corrosion.* 52 (1996) 853.
45. I. Ahamad, S. Khan, K.R. Ansari, M.A. Quraishi, *J. Chem. Pharm. Res.* 3 (2011) 703.
46. A. Singh, V.K. Singh, M.A. Quraish, *J. Mater. Environ. Sci.* 1 (2010) 162.