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Synergic effect between *Argania spinosa* cosmetic oil and *Thymus satureioides* essential oil for the protection of the carbon steel against the corrosion in sulfuric acid medium

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Abstract

The main objective of this work was to study and to compare the inhibition of the corrosion of the Carbon steel,in sulfuric acid medium (0.5 M), using *Thymus satureioides* essential oil (TSEO) mixed with the cosmetic *Arganiaspinosa* oil (CAO) and only CAO.First the composition of the essential oil isolated from the aerial parts of *Thymus satureioides*(TS), an endemic plant from Morocco, was investigated by GC/MS. And then TSEO and CAO were used to evaluate their percentage of the corrosion inhibition. To do this, we used weight loss method, potentiodynamic polarization and impedance spectroscopy (EIS) measurements. The results revealed that TSEOwas found to be rich in monoterpene hydrocarbons and oxygenated monoterpenes, with borneol (32.13 %), α-terpineol (19.87%) and camphene (15.05%) being the major components. Moreover, the TSEO mixed with CAO have a good inhibiting effect on the metal tested in 0.5 M H_2SO_4 solution. The protection efficiency increases with increasing inhibitor concentration to attain, in the presence of CAO+TSEO and CAO respectively 96% at 4g/L and 91% at 5g/L. Potentiodynamic Polarization measurements show also that tested inhibitor acts essentially as a mixed-type inhibitor. The results demonstrated that (CAO+TSEO) is adsorbed on the surface of carbon steel according to Langmuir adsorption isotherm.

1. Introduction

Carbon steel is widely used in most industries, for example in the phosphates industry, thanks to its mechanical properties and availability for the manufacture of reaction vessels such as cooling tower reservoirs, pipelines, etc. [1]. In these industries where sulfuric acid is produced in large quantities or reaction vessels are acid cleaning because of its low cost, Carbon steel reacts easily in ordinary environments containing oxygen. Thus, the study of its corrosion inhibition has attracted much attention. Carbon steel corrosion depends not only on the nature of the environment but also of the condition of use on materials. Most work on carbon steel corrosion reveals that the presence of aggressive elements such as chloride and sulfide accelerates the corrosion of this metal [2-4]. The use of inhibitors is one of the most effective ways to prevent corrosion, especially in acidic media [5]. Large numbers of organic compounds showed significant inhibition efficiency for corrosion of different metals in acidic medium because of the functional group containing hetero-atoms such as nitrogen, sulfur and oxygen [6-11], but most of these compounds are expensive and toxic to living organisms and therefore have a negative impact on the environment [12]. In addition, recent literature is full of researches which test the inhibitory effect of various natural substances against the corrosion of materials. Among the various natural products, such as Argan Hulls [13] *Thymus capitatus* [14,15], black pepper [16], fenugreek [17] *Artemisia* [18], *Hibiscus sabdariffa* [19], for the reason that plant extracts are bio-degradable, safe, environment friendly, easily available and of potentially low cost. Most of the naturally occurring substances are non-toxic and can be extracted by simple process. The anticorrosion effect of cedar oil [20], jojoba oil [21], *Artemisia* oil [22], pennyroyal oil from *Mentha pulegium* [23] eucalyptus oil [24], prickly pear seed oil [25], argan (*Arganiaspinosa* (L.)) extracts [26-28], *Thymus satureoides* [29-30] have been communicated from our laboratories. All of these have been reported to be good inhibitors for metals and alloys in acidic solutions. The encouraging results obtained by cosmetic arganoil and *Thymus satureoides* essential oil as corrosion inhibitor of steel, copper and tinplate in acid solutions permit to test, the synergic effect between cosmetic arganoil (CAO) and *Thymus satureioides*, as an inexpensive, eco-friendly, naturally occurring substance, for the corrosion inhibition of carbon steel in sulfuric acid solution.

The aim of this paper was to study if we add the essential oil of *Thymys saturoides* to *Argania spinosa* cosmetic oil, the inhibition effect of the corrosion will be improved. The electrochemical behavior of carbon steel in 0.5 M H_2SO_4 media in the absence and presence of argan oil has been studied by weight loss measurements, electrochemical techniques potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

There is no report in our knowledge on the effect of the addition of cosmetic argan oil (CAO) mixed to *Thymus satureioides* essential oil on the corrosion of C38E carbon steel in sulfuric acid solution (0.5M H_2SO_4).

2. Experimental and methods

2.1. Plant collection and essential oil extraction

The aerial parts of *Thymus satureioides*, were collected from several regions Argan tree area in Imouzzer Idaoutanane, Agadir Ida Outanane Province, Southwest of Morocco, in June 2013. The taxonomic identification of the species of all samples was confirmed by Pr. Msanda (Laboratory of Biotechnology and Valorization of Natural Resources, Faculty of Sciences, Agadir). The dried plant material was stored in the laboratory at room temperature (298 K) and in the shade before the extraction. The extraction of the essential oil was conducted by hydrodistillation using a Clevenger type apparatus [31]. The essential oil obtained was dried under anhydrous sodium sulfate and stored at 4 °C in the dark before analysis. The botanical name and family of plant sample are summarized in Table 1.

Table 1. The botanical name and family of plant samples

Scientific name	Family	Collection site	Local name	Latitude / longitude	Altitude (m)	EO Yield (% ml/g)	Medicinal use
Thymus satureioides	*Labiatae*	Imouzzer Idaoutanane	Tazouknit	N 00419808/ E 00115089	1568	*3,3±0.02*	Anti-infective expectorant, coughing

2.1. GC-MS analysis

Gas Chromatography-Mass Spectrometry analysis was carried out with a 5973N Agilent apparatus, equipped with a capillary column (95 dimethylpolysiloxane-5% diphenyl), Agilent HP-5MS DI (30 m long and 0.25 mm i.d. with 0.25 urn film thickness). The column temperature program was 60°C during 5 min, with 3°C/min increases to 180°C, then 20°C/min increases to 280°C, which was maintained for 10 min. The carrier gas was helium at a flow-rate of 1 mL/min. Split mode injection (ratio 1:30) was employed. Mass spectra were taken over the m/z 30-500 range with an ionizing voltage of 70 eV. Kovat's retention index was calculated using cochromatographed standard hydrocarbons. The individual compounds were identified by MS and their identity was confirmed by comparison of their RIs, relative to C8-C32 n-alkanes, and mass spectra with those of authentic samples or with data already available in the NIST 2005 Mass Spectral Library and in the literature [32].

2.3 Antioxidant activity

The antioxidant activity in vitro was evaluated by measuring the scavenging power of free radical DPPH (2,2-diphenyl-1-picryhydrazyl) by the essential oils, with some modifications according to [33, 34]. Methanolic solution (500µL) of the essential oil of Thymus satureioides tested at different concentrations (1mg/mL, 0.5mg/mL, 0.25mg/mL, 0.125mg/mL) was mixed with 500 µL of methanolic solution of DPPH (0.004 %). The absorbance is read at 517 nm wavelength after an incubation period of 30 minutes in the dark at ambient temperature. The inhibition of free radical DPPH by BHT (butylhydroxytoluene) and Covi-ox (references antioxidants compounds) was also assessed with the same concentrations and the same conditions for comparison. The inhibition of free radical DPPH percentage (I%) is calculated as follows [34,35]:

$$I\% = 100 \times (A_{control} - A_{test})/A_{control} \qquad (1)$$

Where $A_{control}$ is the absorbance of the control (containing all reagents without the test product) and $A_{test}$is the absorbance of the test compound (containing all reagents and the test product). All tests were performed in triplicate for each concentration [36].

2.4. Corrosion inhibition testing

2.4.1 Solutions preparation

The solution tests were freshly prepared before each experiment by adding the cosmetic argan oil with 2% as percentage by mass of *Thymus satureioides* essential oil directly to the corrosive solution.

2.4.2 Materials and solutions

The steel that we used in this study is a carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (320, 800 and 1200); rinsed with distilled water, degreased in acetone, washed again with bidistilled water and then dried at room temperature before use. The acid solutions (0.5M H2SO4) were prepared by dilution of an analytical reagent grade 98 % H2SO4 with double-distilled water.

2.4.3 Weight loss measurements

This method is a measure of the average corrosion rate. The equipment used is simple. The study is to measure the weight loss of samples surfaces during the time t of immersion of the sample in the corrosive solution maintained at constant temperature. Steel samples of dimensions 1 cm × 1 cm × 0.2 cm. these samples were immersed in 0.5M H2SO4, without and with addition of different concentrations of inhibitor extract. Gravimetric experiments were performed in a double glass cell equipped with a thermostated cooling condenser containing 80 mL non-de-aerated test solution. After immersion, the carbon steel specimens were withdrawn, carefully rinsed with bidistilled water, cleaning ultrasonically in acetone, dried at room temperature, and then weighed. The inhibitory efficiency is determined after 24 hours of immersion, at a temperature of 25°C in atmospheric air. The value of the particular inhibitory effectiveness is the average of three tests under the same conditions for each concentration.

2.4.4. Polarization curves

The electrochemical study is one of the most commonly used techniques to determine a corrosion rate. Indeed, its experimental tests appear to be extremely simple and fast. The method has been used to speed up certain types of corrosion or deterioration. But its main use is for plotting polarization curves. In addition, the program allows voltamaster.4 trace the current logarithmic scale and the use of Tafel method allows us to determine the value of corrosion current and other electrochemical parameters. The current-potential curves were obtained by potentiokinetic mode in the 0.5M H_2SO_4 solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -800 mV to -200 mV versus corrosion potential with a potential scan rate of 1 mV / s. This value is sufficiently low, which allows to approach as much as possible the conditions of the steady state of the system studied. The registration of these curves is done in the direction of increasing potential.

2.4.5 Impedance

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 system impedance is measured as a function of the frequency of the applied signal (between 1 MHz and 100 kHz) and its value is given in the complex plane for each frequency. The resulting Nyquist plot comprises one (or more) semi-circle (s) whose distance to the origin indicates the resistance of the electrolyte and the amplitude indicates the transfer resistance of the electrode For simple systems, the bias resistor can also be obtained by direct reading on the diagram.

3. Results and discussion

3.1. *Thymus satureioides* oil GC-mass spectrum analysis

Thymus satureioides oil analysedby GC-mass spectrum permit the identification of its composition. The essential oil mainly contains bioactive substances: borneol (32.13%), α-terpineol (19.87%), camphene (15.05%), α-pinene (7.85%) and β-cymene (4.90%) (Table 2).

El Bouzidi et al.,[37] was reported that carvacrol (26.5%), followed of borneol (20.1 %) as the most abundant compounds in *T. satureioides*. However, in our study, borneol was current at higher percentage of 32.13%, whereas carvacrol only reached 1.20 % of the total essential oil.

Table 2 . Chemical composition of *Thymus satureioides* essential oil.

Compounds	RT	KI	*T. satureioides* (% of total)
Monoterpenehydrocarbons			**33.94**
Tricyclene	6.77	926	0.54
α-Thujene	6.97	930	0.34
α-Pinene	7.35	939	7.85
Camphene	7.90	954	15.05
Thuja 2,4(10) diene	8.07	960	0.02
Sabinene	8.78	975	0.02
β-Pinene	8.94	978	1.10
Myrcene	9.55	990	0.47
α-Phellandrene	10.06	1002	0.03
δ-3-Carene	10.31	1011	0.01
α-Terpinene	10.63	1017	0.30
p-Cymene	11.15	1024	4.90
Limonene	11.29	1029	1.34
cis-Ocimene	11.64	1037	0.01
γ-Terpinene	12.65	1059	1.74
Terpinolene	13.92	1088	0.22
Oxygenatedmonoterpenes			**61.18**
1,8-Cineole	11.35	1031	0.30
cis-Linalooloxide	13.19	1072	0.03
Camphenilone	13.65	1082	0.01
Linalool	14.72	1096	2.25
cis-*p*-Menth-2-en-1-ol	15.55	1121	0.03
α-Campholenal	15.70	1126	0.02
trans-Pinocarveol	16.43	1139	0.09
Camphor	16.63	1146	1.42
Camphene hydrate	16.74	1149	0.09
Borneol	18.52	1169	**32.13**
Terpinen-4-ol	18.64	1177	1.18
α-Terpineol	19.70	1188	**19.87**
Isobornyl formate	20.69	1239	0.46
Carvacrolmethylether	21.36	1244	0.10
Carvenone	21.95	1258	0.05
Bornylacetate	23.33	1288	1.89
Thymol	23.55	1290	0.06
Carvacrol	24.06	1299	1.20
Sesquiterpenehydrocarbons			**3.56**
α-Copaene	27.06	1376	0.07
β-Bourbonene	27.44	1388	0.06
α-Gurjunene	28.49	1409	0.04

β-Caryophyllene	29.04	1419	2.59
β-Copaene	29.29	1432	0.03
Aromadendrene	29.68	1441	0.04
α-Humulene	30.29	1454	0.11
allo-Aromadendrene	30.57	1460	0.07
γ-Muurolene	31.25	1479	0.06
α-Curcumene	31.52	1480	0.04
Bicyclogermacrene	32.03	1500	0.02
α-Muurolene	32.20	1500	0.04
γ-Cadinene	32.76	1513	0.19
δ-Cadinene	33.13	1523	0.20
Oxygenatedsesquiterpenes			**1.25**
Spathulenol	35.21	1578	0.05
Caryophylleneoxide	35.50	1583	0.75
β-Oplopenone	36.40	1607	0.07
1,10-*diepi*-Cubenol	36.62	1619	0.04
tau-Cadinol	37.62	1640	0.30
α-Cadinol	38.10	1654	0.04
Aromatics			**0.02**
Eugenol	26.86	1359	0.02
Others			**0.02**
3-Octanol	9.72	991	0.02
Total identified			**99.97**

3.2Antioxidant activity

The inhibition percentage of free radical for the studied TSEO was slightly lower than that of BHT and CovioxT-50 for all concentrations used. For example, a concentration of 0.25 mg/mL of essential oil, showed a percentage inhibition of 23 ± 0.1 % while BHT and CovioxT-50 showed a percentage inhibition of 59 ± 0.7 % and 58 ± 0.8 % respectively (Figure 1).

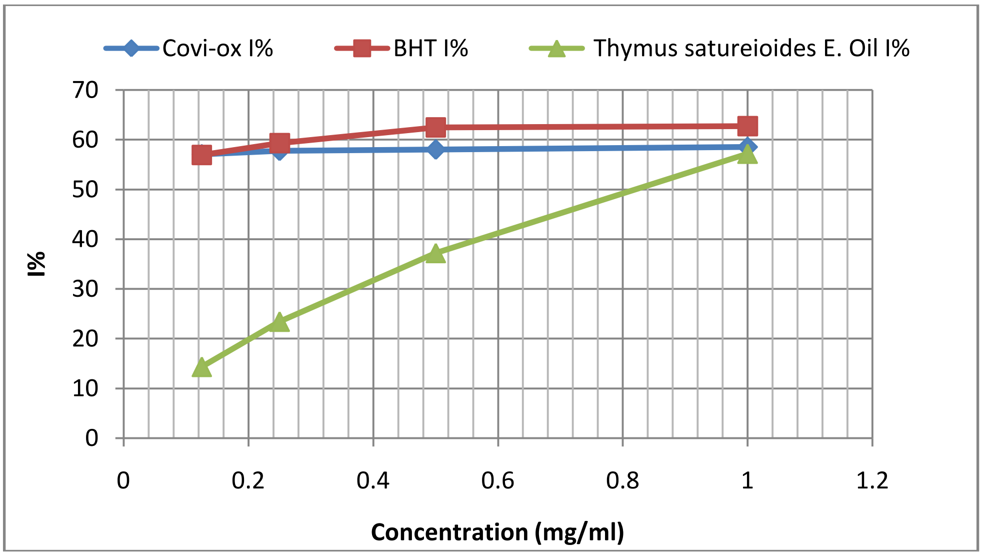

Figure 1: Inhibition percentage of TSEO, Covi-oxT-50 and BHT

We determined graphically the concentration corresponding to 50% inhibition of DPPH (IC50), which characterizes the antioxidant activity of the essential oil studied. The essential oil of TS gave a value of IC$_{50}$ = 0.81 mg/ml and for the reference compounds BHT and Covi-ox was 0.11 mg/mL **(Table 3)**. These results established that BHT has 7.3 times more antioxidant capacity than the essential oil studied.

Table 3. DDPH Scavenging activity (IC50$_{DPPH}$) of *Thymus satureioides* essential oil and the references antioxidants BHT and Covi-oxT-50

Samples	**IC$_{50DPPH}$ (mg/mL)^{a}**
BHT	0.11
Covi-oxT-50	0.11
*Thymus satureioides*EO	0.81

$^{\mathbf{a}}$Values are means (n=3).

The antioxidant activity of several Thymus species essential oils has been already reported [38]. A recent study by El Bouzidi et al., [37] shows that essential oils obtained from tested thymus species prove antioxidant activity by DPPH essay. The most potent oil was obtained from wild *T. maroccanus* (Carvacrol 70.1%, β-Cymene 6.9%, γ-Terpinene 5.9%, α-Pinene 3.3%), but they were less potent than the synthetic antioxidant BHT (IC50 = 4.21 ± 0.08 µg/mL). As a result, this activity has been recognized principally to their content of phenolic components, mainly thymol and carvacrol [39], also, the efficient radical scavenging activity of these compounds is well identified [40], [41]. The high content of carvacrol and/or thymol in *T. maroccanus* and *T. broussonetii* oils reveals their strong antioxidant activity (IC50 = 82.87 ± 2.41 µg/mL and 132.23±3.09, respectively) compared with *T. satureioides* essential oil (IC50 =167.00±2.47), which contained lower levels of these compounds. γ-Terpinene is also characterized by strong antioxidant activity which may be higher than that of phenols, and be due to the presence of activated methylene groups[38, 39]. The other main components, β-cymene, α-pinene, borneol and camphene, have minor or no antioxidant activity. Comparing data, it appears that the antioxidant activity detected in *Thymus satureioides* essential oil is the result of additive, synergistic and/or antagonistic effects between several classes of compounds that they contain.

3.3. Synergic effect between cosmetic il of Argan (CAO) and TSEO

3.3.1. Weight loss, corrosion rates and inhibition percentage

Weight loss measurements of steel were investigated in 0.5M H2SO4 in the absence and presence of various concentrations of inhibitor oil at 6 h of immersion and 298 K.

The inhibitory efficiency (Ew%) of the essential oil is calculated as follows:

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

Where Wcorr and Wcorr(inh) are the corrosion rate of steel in 0.5M H2SO4 in absence and presence of inhibitor, respectively.

The gravimetric trends of the steel immersed in aerated 0.5M H2SO4 in the absence and the presence of the inhibitors at various concentrations are summarized Table 4.

Table 4: Corrosion parameters obtained from weight loss measurements for carbon steel in 0.5M H_2SO_4 containing various concentration of essential oil at 298 K.

Inhibitor	**Concentration (g/l)**	**W_{corr}(mg. cm^{-2})**	**E_w (%)**
Blank	0.0	1.5482	-
CAO	5.0	0.1296	91.63
	4.0	0.1413	90.87
	3.0	0.1864	87.96
	1.0	0.2311	85.07
	0.5	0.2713	82.48
98% CAO+2% Thym	4.0	0.0685	95.57
	3.0	0.0813	94.75
	2.0	0.0894	94.22
	1.0	0.1081	93.02
	0.5	0.1313	91.52

Results of the present investigations involving CAO and 98% CAO+2% TSEO indicate that the inhibition efficiency Ew (%) increases with increasing oil concentration and the maximum inhibition efficiency was obtained with 5g/L and 4g/L concentration of CAO and mixed oil(98% CAO+2% TSEO) respectivelyto achieve 91.63% and 95.57% in the range of concentrations studied. From weight loss measurements, we can conclude that the essential oil studied is the excellent inhibitor.

3.3.2. Potentiodynamic polarization measurements

Potentiodynamic polarisation curves of steel in 0.5M H_2SO_4 in the presence and absence of the tested inhibitors are shown in Figs. 1 and 2. The corrosion parameters including corrosion potential (E_{corr}), current densities (Icorr), cathodicTafel slope (βc), and inhibition efficiency (EI %) are listed in Table 5.

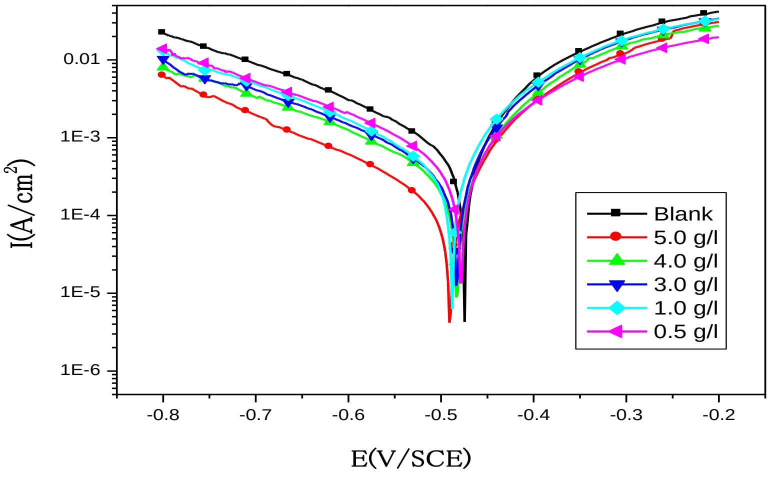

Figure 2: Potentiodynamic polarization curves for carbon steel immersed in 0.5M H_2SO_4 solution in the absence and presence of various concentrations of CAO

The inhibition efficiencyare calculated as follows:

$$E_I\% = (1 - \frac{I'_{corr}}{I_{corr}})x100 \qquad (3)$$

Here, I_{corr} and I'_{corr} are current density in absence and presence of the studied oil respectively. We noted that I_{corr} and I'_{corr} were calculated from the intersection of anodic and cathodicTafel lines.

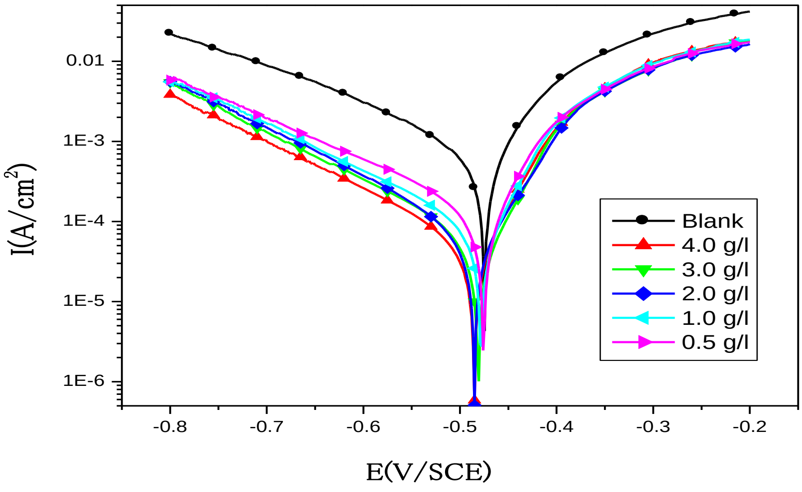

Figure 3: Potentiodynamic polarization curves for carbon steel immersed in 0.5M H_2SO_4 solution in the absence and presence of various concentrations of essential oil CAO+Thym

Table 5 : Data obtained from potentiodynamic polarization measurements of carbon steel immersed in 0.5M H_2SO_4 solution in the absence and presence of various concentrations of inhibitor

Inhibitor	Concentration (g/l)	-Ecorr (mV/SCE)	Icorr (µA/cm2)	-βc (mV/dec)	E_I (%)
Blank	0.0	478	1860	189	-
CAO	5.0	490	159	174	91.45
	4.0	483	367	173	80.27
	3.0	481	459	161	75.32
	1.0	489	600	139	67.74
	0.5	478	670	202	63.98
98 % CAO + 2 % TSEO	4.0	490	62	169	96.67
	3.0	482	70	165	96.24
	2.0	482	90	152	95.16
	1.0	478	96	171	94.84
	0.5	475	144	202	92.26

The Fig. 2 and 3 shows that the addition of (CAO) and (CAO+ TSEO) affects both cathodic reduction reactions and anodic dissolution of steeal and adsorbs in both cathodic and anodic sites of surface steel, indicating that the two natural oils could be classified as mixed-type inhibitors. We remarked that the cathodic current–potential curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled and that the addition of the oils does not modify the mechanism of this process (Fig.2 & 3) [42].The analysis of the electrochemical parameters values given in Table.2, reveal that, inhibition efficiency increases with an increase of the concentration of natural oils. The maximum inhibition efficiency observed at higher inhibitor concentration indicates that more inhibitor molecules are adsorbed on the metal surface. We note that the corrosion current densities were more significantly reduced in the presence of the synergy of CAO and TSEO than CAO. The best efficiencies obtained in the presence of CAO+Thym and CAO respectively are 96% at 4g/L and 91% at 5g/L.

3.3.3. Electrochemical impedance spectroscopy measurements (EIS)

The corrosion behavior of carbon steel, in 0.5M H_2SO_4 solution in the absence and presence of cosmeticarganoil and (CAO + TSEO), was also investigated by electrochemical impedance spectroscopy measurements method at 298K after 30 min of immersion.

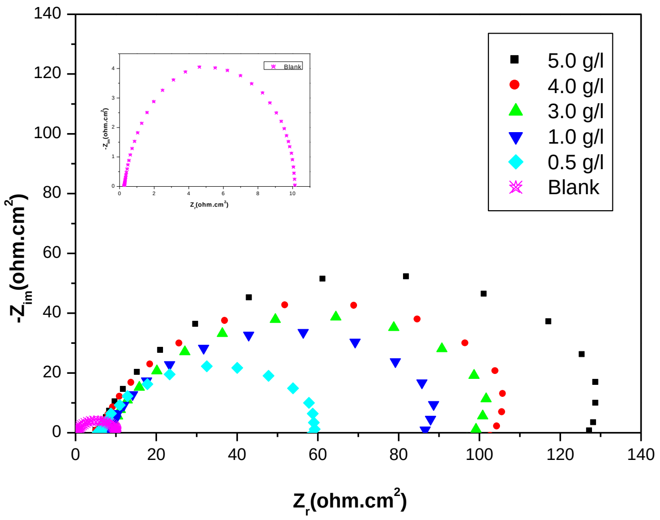

Figure 4: Nyquist plots for carbon steel immersed in 0.5M H_2SO_4 solution in the absence and presence of various concentrations of (CAO)

We note, for all concentrations used, the presence of a single capacitive loop corresponding to the charge transfer resistance. From these diagrams made to potential abandonment, we could access to the values of Rct charge transfer resistance and the ability to the double layer Cdl and therefore to the inhibitory efficiency of oils studied in the operating conditions used.

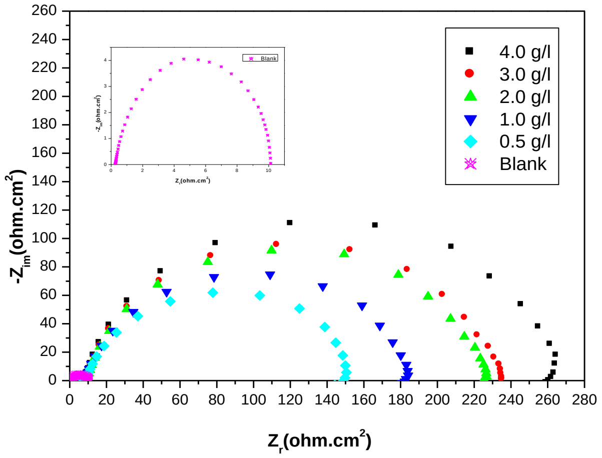

Figure 5: Nyquist plots for carbon steel immersed in 0.5M H_2SO_4 solution in the absence and presence of various concentrations of (CAO+TSEO).

Charge transfer resistance values are calculated from the difference impedance of the high and low frequency on the real axis, as suggested by Tsuru et al., [43].

The inhibition efficiency of the steel corrosion is calculated from the charge transfer resistance according to the equation:

$$E_{Rct}\% = \frac{(R_{ct} - R^{\circ}_{ct})}{R_{ct}} x100 \qquad (4)$$

Were R_{ct} and R^0_{ct} are the charge transfer resistances in inhibited and uninhibited solutions respectively.

The electrochemical impedance parameters derived from these investigations are mentioned in Table 6.

Table 6: Data from electrochemical impedance spectroscopy measurements of carbon steel in 0.5M H_2SO_4 solution in the absence and presence of various concentrations of tested inhibitors

Concentration (M)	**Concentration (g/l)**	**$Rc_t(\Omega.cm^2)$**	**$C_{dl}(\mu F.cm^{-2})$**	**E_{Rct} (%)**
Blank	0.0	10	100	-
	5.0	127	79.35	92.12
	4.0	104	96.90	90.38
CAO	3.0	99	101.80	89.89
	1.0	86	117.18	88.37
	0.5	59	170.81	83.05
	4.0	260	97.21	96.15
	3.0	235	107.55	95.74
98% CAO+2% Thym	2.0	226	111.84	95.57
	1.0	184	137.36	94.56
	0.5	150	168.50	93.33

The R_{ct} values increased with the increase of the concentration of argan oil. 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 results obtained from the polarization technique in acidic solution were in good agreement with those obtained from the electrochemical impedance spectroscopy (EIS). From Table 6, it is clear that the R_{ct} values increased and that the C_{dl} values decreased with increasing inhibitor concentration. These results indicate a decrease in the active surface area caused by the adsorption of the inhibitors on the carbon steel surface, and it suggests that the corrosion process became hindered [44]. The best efficiencies obtained in the presence of (CAO+TSEO) and (CAO) respectively are 96% at 4g/L and 92% at 5g/L. The presence of the essential oils lead to significant effects: the charge transfer resistance significantly increases, and the C_{dl} decreases, in the presence of the essential oil, which may be caused by reduction in the local dielectric constant and/or by an increase in the thickness of the electrical double-layer. These results show that the presence of the essential oils modifies the electric double-layer structure suggesting that the inhibitor molecules act by adsorption at the metal/solution interface. Moreover, C_{dl}

decreases with increase of the concentration of inhibitor. This phenomenon is generally related to the adsorption of organic molecules on the metal surface and then leads to a decrease in the dielectric constant and/or an increase in the thickness of the electrical double layer [45, 46].

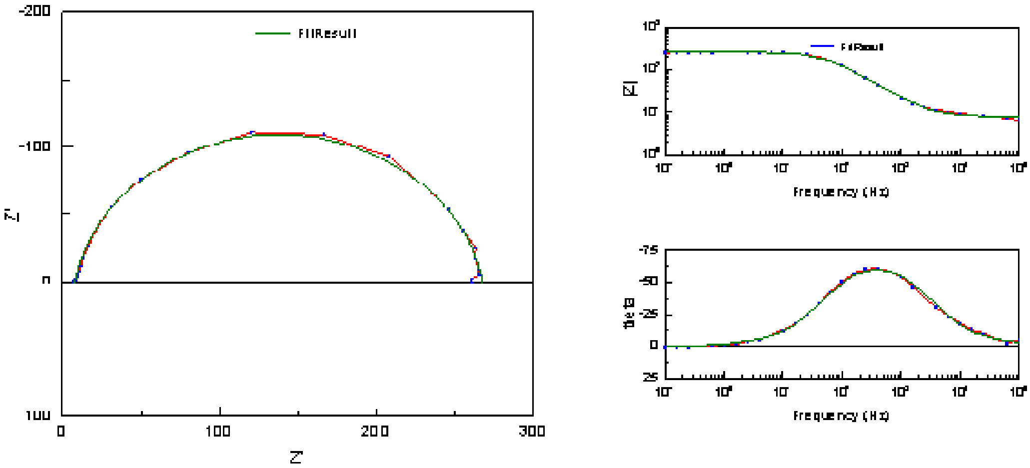

Figure 6: EIS Nyquist (a) and Bode (b) plots for carbon steel / 0.5M H_2SO_4+ 4g/l of (CAO+Thym) interface

Excellent fit with this model was obtained with our experimental data (Fig. 6). It is observed that the fitted data match the experimental, with an average error of about 0.01%. R_t values were simultaneously determined by analysis of the complex-plane impedance plots and the equivalent circuit model and the result are very similar with insignificant changes. The impedance spectra with one capacitive loop were analyzed by using the circuit in Fig. 6 and the values of the double–layer capacitance C_{dl} were calculated from the frequency at which the impedance imaginary component $-Z_i$ is maximum using the equation:

$$f(-Zi_{max}) = \frac{1}{2\pi C_{dl} R_t} \qquad (5)$$

With Cdl : Double layer capacitance ($\mu F.cm^{-2}$) ; f_{max} : maximum frequency (Hz) and Rct : Charge transfer resistance ($\Omega.Cm^2$)

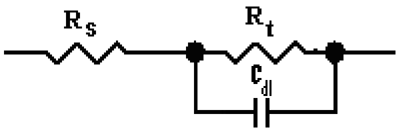

Figure 7: The electrochemical equivalent circuit used to fit the impedance spectra

3.4. Adsorption considerations

The adsorption isotherm reveals more information on the interaction between the metal surface and the inhibitor essential oils**.** Fig.6 shows the linear dependence of C/θ as a function of concentration C of inhibitors where θ is the surface coverage. The degree of surface coverage (θ) at different concentrations of the inhibitor in 0.5M H_2SO_4 were evaluated from weight loss measures using the flowing formula: $\theta = E_W(\%)/100$ (6)
Inhibitor adsorbs on the steel surface according to the Langmuir kind isotherm model which obeys the relation [47]:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (7)$$

K is the equilibrium constant of the adsorption process.

The Fig. 8 (plot of C/θ versus C) gives straight line with slope near to 1, meaning that the adsorption of the inhibitor under consideration on carbon steel / acidic solution interface obeys Langmuir's adsorption.
The literature shows that the adsorption of organic compounds occurs with the aromatic rings mostly adsorbed perpendicular with respect of the metal surface at low concentration, but at high inhibitor concentration the molecules are reoriented to the parallel mod [48]. Furthermore, the adsorption phenomenon may be made by the principal constituent of the essential oils. But as the natural oil contains many components, the inhibitory action may be due to synergistic intermolecular of the active molecules of these oils [].

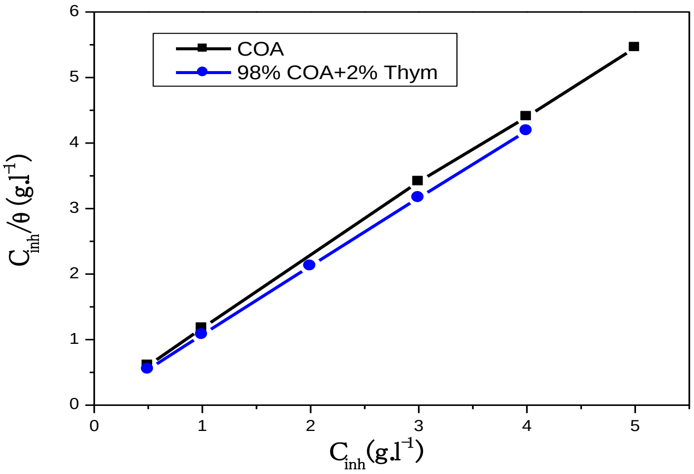

Figure 8: Langmuir adsorption of essential oil on the carbon steel surface in 0.5M H_2SO_4 solution at 298K

4. General discussion

In a recent study [29], the essential oil of *Thymus satureoides* (35.89% of borneol) proved to be an effective inhibitor for the corrosion of copper in 2M HNO_3, and physisorbed onto the surface of copper according to the Langmuir isotherm model. The study also showed that addition of the essential oil of *Thymus satureoides* has a more pronounced effect (89.02% at 1200 pp) than that of its major constituent, borneol alone (69.72% at 1600 ppm). Therefore, this activity is mainly due to a synergy between the chemicals constituting the *Thymus satureoides* oil, and not just to its major constituent (borneol) alone. In addition, the present work shows that the protection efficiency of(CAO+TSEO) (96% at 4g/L) is better than this presented by only (CAO)(91% at 5g/L).As a result,the tested inhibitor (CAO + TSEO) proves to be an effective protector for the corrosion of carbon steel because of the synergy between their compounds.

Conclusion

Chemical analysis shows that the major constituents of *Thymus satureioides* essential oil (TSEO) were borneol (32.13 %), α-terpineol (19.87%) and camphene (15.05%).The antioxidant activity detected in (TSEO) by DPPH essay is the product of additive, synergic and/or antagonistic effects, as this essential oil contain several classes of compounds. Results obtained through weight loss measurements and electrochemical tests demonstrated that (CAO+TSEO) act as efficient corrosion inhibitors of the carbon steel in 0.5M H_2SO_4 solution. The corrosion process was inhibited by adsorption of the organic matter on the mild steel surface. Inhibition efficiency increases with increased concentration of the tested inhibitors and the inhibition efficiency of the synergy between (CAO) and (TSEO)is higher than this presented by only (CAO).The decrease in the charge transfer resistance with the increase in the inhibitor concentration, showed that (CAO+TSEO)formed protective layers on the carbon steel surface. Tafel polarization measurements show that (CAO + TSEO) act essentially as a mixed type inhibitor.

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