Int. J. Electrochem. Sci., 8 **(2013)** 11896 - 11915

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Application of *Senecio Inaequidens* Essential Oil and Its Fractions as Eco-friendly Inhibitors of Mild Steel Corrosion in 1M HCl Solution

S. Andreani[1], *M. Znini*[2], *Paolini*[1], *L. Majidi*[2,*], *B. Hammouti*[3], *J. Costa*[1], *A. Muselli*[1]

[1]Université de Corse, UMR CNRS 6134, Laboratoire de Chimie des Produits Naturels, Faculté des Sciences et Techniques, Corse, France.
[2]Université My Ismail, Laboratoire des Substances Naturelles & Synthèse et Dynamique Moléculaire, Faculté des Sciences et Techniques, Errachidia, Morocco.
[3]Université Mohamed Premier, Laboratoire de Chimie Appliquée et Environnement, Faculté des Sciences, Oujda, Morocco.
[*]E-mail: lmajidi@yahoo.fr

Received: 2 June 2013 / *Accepted:* 26 July 2013 / *Published:* 10 September 2013

The chemical composition of *Senecio inaequidens* essential oil was investigated for the first time using Gas chromatography (GC), Gas chromatography/Mass spectrometry (GC/MS) and Nuclear Magnetic Resonance (NMR) after column chromatography (CC). Sixty components accounting for 98.8 % of the oil were identified. Among them, myrcene (21.4 %), *(Z)*-β-ocimene (17.6 %), α-pinene (12.5 %), limonene (8.1 %) and cacalohastine (6.8 %) are the main components. The inhibitions of the corrosion of mild steel in Hydrochloric acid solution by *S. inaequidens* essential oil and its CC-fractions have been studied using weight loss measurements. All samples showed promising anticorrossive activity against mild steel in 1M HCl. Inhibition was found to increase with increasing concentration of all samples to attain 90.56 %, 82.54 %, 86.54 % and 87.14 % at 2g/L for *S. inaequidens* oil, hydrocarbon fraction (HF) and oxygenated fractions (OF and OF1), respectively. The effect of temperature on the corrosion behavior of mild steel in 1 M HCl without and with the *S. inaequidens* essential oil at 2 g/L was also studied. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the mild steel surface according to the Langmuir adsorption isotherm. The thermodynamic parameters for activation and adsorption processes were calculated and discussed. The results obtained showed that the *S. inaequidens* essential oil could serve as an environmentally inhibitor of the corrosion of mild steel in Hydrochloric acid media.

Keywords: Adsorption, Corrosion Inhibition, Essential oil, Mild steel, *Senecio inaequidens*

1. INTRODUCTION

Hydrochloric acid is one of the most widely used acids for removal of undesirable scale and rust in mild steel finishing industries, cleaning of boilers, acid pickling and heat exchangers. Also, steel has found wide applications in a broad spectrum of industries and machinery; however its tendency to corrosion made it not the adequate for exposures in contact with aggressive acids [1]. The use of inhibitors is one of the best options of protecting metals against corrosion. Several inhibitors in used are either synthesized from cheap raw material or chosen compounds having hetero atoms in their aromatic or long chain carbon system [2]. However, most of these inhibitors are highly toxic to cause severe hazards to both human beings and the environment during its application [3]. Thus, the researchers have been focused on the use of eco-friendly compounds and ecologically acceptable such as extract of common plants because to bio-degrability, eco-friendliness, low cost and easy availability and renewable sources of materials [4].

The recent trend is to save human being and environment by using eco-friendly inhibitors. Some investigators studied the plant extract, especially essential oils, become more important as an environmentally being, readily available, renewable and acceptable source for a wide range of inhibitors [5]. The essential oils are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as "Green Inhibitors". In this context, in our laboratory, much work has been conducted to study the inhibition by some essential oils on the corrosion of steel in acidic media. It has been reported that the essential oils of *Salvia aucheri* var. *mesatlantica* [6], *Jojoba* [7], *Euphorbia falcata* [8], *Lavandula multifida* [9], *Pennyroyal* [10], *Mentha pulegium* [11], *Eucalyptus globulus* [12], *Artemisia herba-alba* [13], *Cedrus atlantica* [14] and *Foeniculum vulgaris* [15] have been found to be very efficient corrosion inhibitors for mild steel in HCl and H_2SO_4 media. In order to extend the earlier work, essential oil of *Senecio inaequidens* is chosen to use as the corrosion inhibitor on mild steel in 1M HCl media.

Senecio inaequidens (SI), family of *Asteraceae* is a perennial plant 20-100 cm high with leaves 4-10 cm long and yellow flower heads 8-10 mm present from March to December [16]. It is a plant native of South Africa considered as an invasive species in several countries. Its introduction in Europe would date of the years 30 probably with the wool trade from South Africa. In Corsica, the plant was listed in two locations (Arro and Calvi) where it monitored and annually ripped by the "Conservatoire Botanique Nationale de la Corse" [17]. Phytochemical investigation of *S. inaequidens* were recently reviewed [18] and pyrolizidic alkaloid compounds, eremophilane, furanoeremophilane and polyphenolic compounds were reported in the solvent extracts of the plant. Anti-oxidant, antidiabetic and cytotoxic properties [19], as well as antibacterial and antifungal activities of the methanolic extract of the plant [20] have been described. However to the best of our knowledge no study reports the chemical composition of the essential oil of *S. inaequidens*.

The aim of the present work is to study the inhibitive action of *S. inaequidens* essential oil and its CC-fractions as cheap, green and naturally occurring substances on corrosion behavior of mild steel in 1 M HCl solution using weight loss measurements. In this case, the chemical composition of the essential oil from Corsica was investigated using GC, GC/MS and NMR analysis after successive CC,

the effect of concentration and temperature on the inhibition efficiency has been examined and the thermodynamic parameters for activation and adsorption processes were calculated and discussed.

2. EXPERIMENTAL PART

2.1. Plant material and essential oil isolation

The aerial parts of *S. inaequidens* were harvested from April 2012 (full bloom) from 2 localities of Corsica (France): Calvi (S1: 42°33'17.37"N; 8°45'50.74"E) and Arro (S2: 42°05'31.29"N; 8°48'29.86"E). Voucher specimens were deposited in the herbarium of University of Corsica, Corte, France. For both sample locations, the fresh plant material (600-1800 g) was water-distillated (5 h) using a Clevenger-type apparatus according to the method recommended in the European Pharmacopoeia [21].

2.2 Oil fractionation

S. inaequidens collective oil (EO) investigated in the present study, was obtained by the pooling of both individual essential oils originated from Calvi and Arro (Corsica, France). 14 g of the (EO) sample were submitted of chromatography on a silica gel column CS (200-500 μm), 40 g (Clarisep® Bonna Agela Technologies, Willington, USA) with a Combi Flash apparatus (Teledyne ISCO, Lincoln, USA) equipped with a fraction collector monitored by an UV-detector. A hydrocarbon fraction (HF: 11.25 g) was obtained by elution with hexane (n-C_6H_{14}) and an oxygenated fraction OF (1.65 g) was obtained by elution with diisopropyl oxide ($C_6H_{14}O$). 1.5 g of OF was further chromatographed with same apparatus on a silica gel column CS (200-500 μm), 12 g (Clarisep® Bonna Agela Technologies, Willington, USA). Three polar sub-fractions, OF1 (1085.0 mg), OF2 (88.3 mg) and OF3 (176.7 mg) were obtained using an elution of 99/1, 97/3 and 0/100 (n-C_6H_{14}/ $C_6H_{14}O$, v/v), respectively. OE, HF, OF and OF1 samples were used to study the inhibitive action on corrosion.

2.3. Gas Chromatography

GC analyses were carried out using a Perkin Elmer Clarus 600 GC apparatus (Walton, MA, USA) equipped with a single injector and two flame ionization detectors (FID). The apparatus was used for simultaneous sampling to two fused-silica capillary columns (60 m x 0.22 mm, film thickness 0.25 μm) with different stationary phases: Rtx-1 (polydimethylsiloxane) and Rtx-Wax (polyethylene glycol). Temperature program: 60 to 230 °C at 2 °C.min^{-1} and then held isothermal 230 °C (30 min). Carrier gas: hydrogen (1 mL.min^{-1}). Injector and detector temperatures were held at 280 °C. Split injection was conducted with a ratio split of 1:80. Injected volume on each column: 0.1 μL.

2.4. Gas Chromatography-Mass Spectrometry

The oils and the fractions obtained by CC were investigated using a Perkin Elmer TurboMass quadrupole detector, directly coupled to a Perkin Elmer AutoSystem XL (Walton, MA, USA) equipped with two fused-silica capillary columns (60 m x 0.22 mm, film thickness 0.25 μm), Rtx-1 (polydimethylsiloxane) and Rtx-Wax (polyethylene glycol). Both columns were used with the same MS detector. Oil analyses were consecutively carried out on apolar then on polar column. For each sample, two reconstructed chromatograms (RIC) were provided and they have been investigated consecutively. Other GC conditions were the same as described above. Ion source temperature: 150 °C; energy ionization: 70 eV; electron ionization mass spectra were acquired with a mass range of 35 – 350 uma during a scan time 1 s. Oil injected volume: 0.1 μL, fraction injected volume: 0.2 μL.

2.5. Component Identification and Quantification

Identification of individual components was based i) on comparison of calculated retention indices (RI), on polar and apolar columns, with those of authentic compounds or literature data [22]; ii) on computer matching with commercial mass spectral libraries and comparison of mass spectra with those of our own library of authentic compounds or literature data [22-25]. The quantification of the *S. inaequidens* essential oil components was performed using methodology reported by Bicchi et al. [26] and adapted by our laboratory [27]. Component quantification was carried out using peak normalization, including FID response factors (RFs) relative to tridecane (0.7 g/100g) used as internal standard and expressed as normalized % abundance.

2.6. NMR analysis

^{1}H, ^{13}C-NMR and DEPT were performed using a Bruker Avance 400 Fourier Transform spectrometer (Wissembourg, France) operating at 100.13 MHz for ^{13}C-NMR and 400.52 MHz for ^{1}H-NMR and equipped with a 5 mm probe. Spectra were measured in deuterated chloroform and all shifts were referred to the internal standard tetramethylsilane (TMS). ^{13}C-NMR spectra were recorded with the following parameters: pulse width, 4 s (flip angle, 45°); acquisition time, 2.7 s for 128 K Data table 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 3000–5000 for each sample depending of the amount of product. The ^{1}H-NMR spectra were recorded with the following parameters: flip angle, 30°; acquisition time, 2.56 s for 32,000 data table with a spectral width of 7 000 Hz (17.5 ppm).

2.7. Corrosion test

2.7.1. Preparation of materials

The aggressive solutions of 1 M HCl was prepared by dilution of AR grade 37% HCl with distilled water. The material used in this study was mild steel (2 cm x 2 cm x 0.05 cm) 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 the remainder iron (Fe). For all the experiments, the mild steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (grades 400, 600 and 1200), then washed thoroughly with double-distilled water, degreased with AR grade ethanol, and finally dried at room temperature before use.

2.7.2. Weight loss measurements

2.7.2.1. Effect of concentration of S. inaequidens essential oil and its fractions

Weight loss tests 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 SI essential oil and its fractions ranging from 0.25 to 2 g/L. 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. Triplicate experiments were performed in each case and the mean value of the weight loss is reported using an analytical balance (precision ± 0.1 mg). Weight loss allowed us to calculate the mean corrosion rate as expressed in $mg.cm^{-2}\ h^{-1}$.

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

$$W = \frac{\Delta m}{St} \qquad (1)$$

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

where Δm (mg) is the specimen weight before and after immersion in the tested solution, W_{corr} and $W_{corr(inh)}$ are the values of corrosion weight losses ($mg/cm^2.h$) 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).

2.7.2.2. 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 [28]. The change of the corrosion rate with the temperature was studied in 1 M HCl during 1 h of immersion, both in the absence and presence of inhibitors at a concentration corresponding to the maximum inhibition efficiency. For this purpose, gravimetric experiments were performed at different temperatures (303–343 K).

To calculate activation thermodynamic parameters of the corrosion process, Arrhenius Eq. (3) and transition state Eq. (4) were used [29]:

$$W = A\exp\left(-\frac{E_a^{\circ}}{RT}\right) \qquad (3)$$

$$W = \frac{RT}{Nh}\exp(\frac{\Delta S_a^\circ}{R})\exp(-\frac{\Delta H_a^\circ}{RT}) \qquad (4)$$

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, $\Delta S°_a$ is the entropy of activation and $\Delta H°_a$ is the enthalpy of activation.

2.7.3. Adsorption isotherm

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of the inhibitors must be calculated with several adsorption isotherms, including Langmuir, Frumkin, and Temkin. In this study, the degree of surface coverage values (θ) for various concentrations of the inhibitor in acidic media have been evaluated from the Weight loss measurements.

3. RESULTS AND DISCUSSION

3.1. Essential oil composition

Preliminary analyses of *S. inaequidens* essential oils from Calvi and Arro were performed. Both essential oil samples exhibited close GC chromatograms and consequently, they were pooled to produce *S. inaequidens* "collective oil" (OE) in order to perform detailed analysis using successive fractionations, GC, GC/MS and NMR. Integrated analysis of the OE sample allowed identifying sixty components which accounted to 98.7 % of the total amount. Among them, 30 monoterpenes, 21 sesquiterpenes, 7 non terpenic compounds and 2 phenylpropanoids were identified. The essential oil was dominated by hydrocarbon compounds (87.5 %) while oxygenated compounds accounted for 11.2 % of the oil. Among them, hydrocarbon monoterpenes (77.6 %) and non terpenic compounds (7.4 %) were higher. The other classes of compounds amounted for never more than 7.3 %. The main components were myrcene **8** (21.4 %), (Z)-β-ocimene **13** (17.6 %), α-pinene **5** (12.5 %), limonene **12** (8.1 %) and **59** (6.8 %). The identification of 56 components was performed by comparison of their EI-MS and retention indices with those of own library, three by comparison with data from commercial libraries and the identification of **59** was performed by GC/MS and NMR. Successive fractionations of the *S. inaequidens* essential oil allowed to concentrating the unidentified component **59** close to purity (99.7 %) in OF1 fraction. ^{1}H and ^{13}C-NMR chemical shifts of 59 acquired from OF1 fraction matched with those of cacalohastine reported in the literature [30]. This benzofurane derivative was firstly identified as solvent extract component of *Cacalia hastata roots* [31], *Senecio canescens* syn. *Calcitium canescens* [32,33] and *S. lydenburgensi* [34]. It was also identified as essential oil component of *Cacalia hastata var orientalis* [30] but to our knowledge, this study is the first report of cacalohastine **59** as oil component of *Senecio* genus.

Table 1. Chemical compositions of *S. inaequidens* essentials oils, fractions and sub-fractions.

No[a]	Components[b]	LRIia[c]	RIa[d]	RIp[e]	Rf [f]	EO[g]	FH [h]	OF [h]	OF1[h]	Identification[i]
1	heptene	680	686	721	1.00	0.3	0.5	-	-	RI, MS
2	octene	788	770	805	1.00	0.7	1.0	-	-	RI, MS
3	nonene	837	887	932	1.00	1.6	2.0	-	-	RI, MS
4	*α*-thujene	932	924	1023	1.01	1.3	1.8	-	-	RI, MS
5	*α*-pinene	936	933	1019	1.01	12.5	1.4	-	-	RI, MS
6	sabinene	973	967	1120	1.01	3.2	4.2	-	-	RI, MS
7	*β*-pinene	978	973	1110	1.01	3.2	4.0	-	-	RI, MS
8	myrcene	987	985	1159	1.01	21.4	21.6	-	-	RI, MS
9	*α*-phellandrene	1002	1000	1166	1.01	1.0	2.1	-	-	RI, MS
10	*α*-terpinene	1013	1011	1177	1.01	1.1	1.8	-	-	RI, MS
11	*p*-cymene	1015	1014	1268	0.93	0.9	1.3	-	-	RI, MS
12	limonene	1025	1024	1199	1.01	8.1	9.2	-	-	RI, MS
13	*(Z)*-*β*-ocimene	1029	1030	1230	1.01	17.6	18.0	-	-	RI, MS
14	*(E)*-*β*-ocimene	1041	1040	1247	1.01	4.2	4.8	-	-	RI, MS
15	*γ*-terpinene	1051	1051	1248	1.01	0.8	1.2	-	-	RI, MS
16	fenchone	1069	1073	1406	1.31	0.1	-	0.5	-	RI, MS
17	terpinolene	1082	1081	1279	1.01	1.7	1.4	-	-	RI, MS
18	*allo*-ocimene	1126	1120	1375	1.01	0.6	0.8	-	-	RI, MS
19	*β*-thujone	1103	1100	1425	1.31	0.1	-	0.2	-	RI, MS
20	*α*-camphonelal	1105	1105	1481	1.40	0.1	-	0.2	-	RI, MS
21	*(Z)*-ocimene oxide	1115	1115	1498	1.24	0.1	-	0.1	-	RI, MS, ref
22	*(Z)*-limonene-1,2-epoxide	1126	1119	1450	1.24	0.4	-	0.2	-	RI, MS
23	*(E)*-limonene-1,2-epoxide	1130	1123	1450	1.24	0.1	-	0.4	-	RI, MS
24	lyratol	1152	1145	1791	1.34	0.1	-	1.5	-	RI, MS
25	albene	1154	1152	1287	1.01	0.2	0.5	-	-	RI, MS
26	terpinen-4-ol	1164	1170	1592	1.34	0.5	-	1.5	-	RI, MS
27	octyl acetate	1188	1179	1492	1.55	0.1	-	0.1	-	RI, MS, ref
28	dodecanal	1180	1185	1495	1.40	0.1	-	0.1	-	RI, MS
29	carvone	1214	1217	1745	1.31	0.1	-	0.3	-	RI, MS
30	*trans*-pinocarvyl acetate	1287	1275	1752	1.55	0.1	-	0.2	-	RI, MS, ref
31	methyl geraniate	1306	1305	1684	1.55	0.1	-	0.1	-	RI, MS
32	myrtenyl acetate	1313	1307	1682	1.55	0.1	-	0.1	-	RI, MS
33	*(E)*-carvyl acetate	1318	1309	1742	1.55	0.1	-	0.1	-	RI, MS
34	myrcenyl acetate	1330	1327	1721	1.55	0.1	-	0.3	-	RI, MS
35	*(Z)*-carvyl acetate	1345	1334	1874	1.55	0.1	-	0.2	-	RI, MS
36	eugenol	1331	1336	2180	1.34	0.2	-	0.4	-	RI, MS
37	neryl acetate	1342	1345	1732	1.55	0.3	-	0.2	-	RI, MS
38	methyl eugenol	1369	1373	2012	1.34	0.1	-	1.4	-	RI, MS
39	*β*-elemene	1389	1387	1589	1.00	0.5	0.8	-	-	RI, MS

40	*(E)-β*-caryophyllene	1421	1417	1600	1.00	1.3	2.1	-	-	RI, MS
41	*α*-humulene	1455	1450	1671	1.00	2.5	2.5	-	-	RI, MS
42	*γ*-curcumene	1473	1469	1774	1.00	0.1	0.5	-	-	RI, MS
43	*γ*-muurolene	1474	1469	1681	1.00	0.6	0.8	-	-	RI, MS
44	germacrene-D	1479	1475	1712	1.00	0.1	0.3	-	-	RI, MS
45	*γ*-himachalene	1479	1479	1695	1.00	0.1	0.3	-	-	RI, MS
46	*β*-selinene	1486	1483	1721	1.00	0.1	0.3	-	-	RI, MS
47	4-*epi*-*cis*-dehydroagorafurane	1490	1485	1718	1.41	0.1	-	1.3	-	RI, MS
48	bicyclogermacrene	1494	1491	1732	1.00	1.6	1.8	-	-	RI, MS
49	*β*-bisabolene	1503	1500	1724	1.00	0.1	0.2	-	-	RI, MS
50	δ-cadinene	1520	1513	1761	1.00	0.1	0.3	-	-	RI, MS
51	*(E)*-nerolidol	1553	1551	2041	1.34	0.1	-	0.3	-	RI, MS
52	spathulenol	1572	1563	2123	1.34	0.3	-	5.7	-	RI, MS
53	caryophyllene oxide	1578	1568	1985	1.41	0.3	-	3.5	-	RI, MS
54	viridiflorol	1592	1590	2092	1.34	0.1	-	0.6	-	RI, MS
55	humulene epoxide II	1602	1600	2052	1.41	0.1	-	0.5	-	RI, MS
56	1,10 *diepi*-cubenol	1615	1612	2039	1.34	0.1	-	0.1	-	RI, MS
57	α-acorenol	1620	1646	2132	1.34	0.1	-	0.5	-	RI, MS
58	aromadendrene oxide II	1624	1619	1995	1.41	0.1	-	0.3	-	RI, MS
59	cacalohastine	-	2004	2761	1.41	6.8	-	72.8	99.7	RI, MS, NMR
60	cacalol	2070	2070	2712	1.34	0.1	-	1.3	-	RI, MS
Total identification (%)						98.7	99.1	95.0	99.7	
	Classes of compounds									
	Hydrocarbon compounds					87.5	99.1	-	-	
	Oxygenated compounds					11.2	-	95.0	99.7	
	Hydrocarbon monoterpenes					77.6	85.2	-	-	
	Hydrocarbon sesquiterpenes					7.3	10.4	-	-	
	Other hydrocarbon compounds					2.6	3.5	-	-	
	Oxygenated monoterpenes					2.5	-	6.1	-	
	Oxygenated sesquiterpenes					1.3	-	12.8	-	
	Other oxygenated compounds					7.4	-	76.1	99.7	

[a] Order of elution is given on apolar coloumn (Rtx-1)

[b] Normalized % abundances of oil are given on the apolar column

[c] Retention indices from literature on the apolar column reported from [22]

[d] Retention indices on the Rtx-1 apolar column

[e] Retention indices on the Rtx-wax polar column

[f] Response factors (Rf) for the calculation mode see experimental section

[g] EO: Collective essential oil of *S.inaequidens*

[h] Fractions of the essential oil obtained by CC, HF: hydrocarbon fraction; OF, OF1: Oxygenated fractions, obtained using elution gradient C_6H_{14}/Et_2O; 100/0%; 0/100%; 99/1%; respectively

[i] RI, Retention indices; MS, mass spectra in electronic impact mode; NMR spectra of C^{13} and H^{1}
Ref., compounds 21, 27, 30 were identified from commercial data libraries [22].

3.2. Corrosion tests

3.2.1. Effect of Inhibitor Concentration

The values of percentage inhibition efficiency E_w (%) and corrosion rate (W) obtained from weight loss method at different concentrations of SI essential oil at 298 K are summarized in Table 2 and Fig. 1.

Table 2. Gravimetric results of mild steel in acid without and with addition of the *S. inaequidens* essential oil at various contents (*t*= 6h, *T*= 298 K).

Inhibitor	C (g/L)	W (mg/h.cm^2)	E_w (%)
SI essential oil	0	0.381	--
	0.25	0.193	49.36
	0.5	0.165	56.6
	1	0.101	73.53
	1.5	0.056	85.28
	2	0.036	90.56

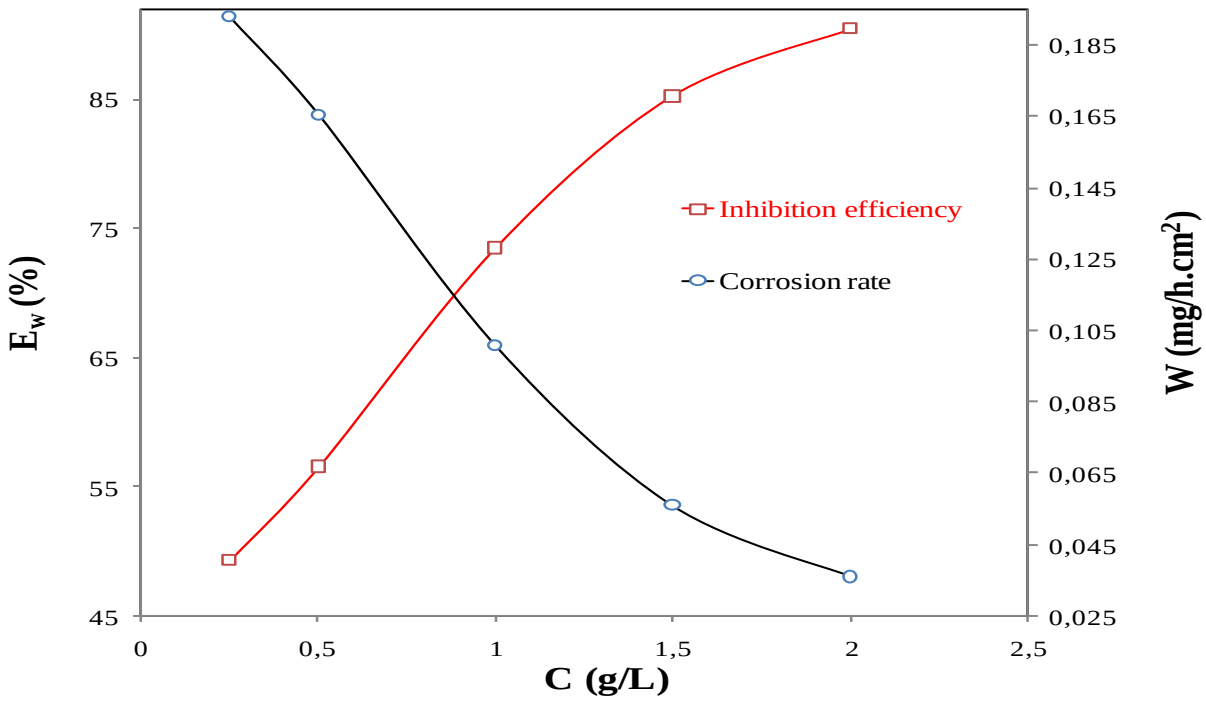


Figure 1. Variation of corrosion rate (W) and inhibition efficiency (E_w) of corrosion of mild steel in 1 M HCl with different concentration of *S. inaequidens* essential oil.

The results shows that the corrosion rate (W) decreases noticeably with the inhibitor concentration from 0.381 to 0.036 mg cm^{-2} h^{-1} at 0 and 2 g/L of SI essential oil, respectively, i.e. the

corrosion inhibition enhances with the inhibitor concentration. This behavior is due to the fact that the adsorption coverage of inhibitor on mild steel surface increases with the inhibitor concentration [35]. It is clear also that the inhibition efficiency E_w (%) increases sharply with increase in concentration of SI essential oil. The maximum E_w is 73.53 % at 1 g/L and the inhibition is estimated to be higher than 80 % even at 1.5 g/L, and its protection is ≥ 90% at 2 g/L, which indicates that SI essential oil is a good inhibitor for mid steel in 1 M HCl solution. Under similar conditions, E_w lavender oil is 90% at 2 g/L [36]. Therefore, comparing with some essential oils such as *Mentha pulegium* (80% at 2.76 g/L) [10], *Eucalyptus globulus* (72 % at 3 mL/L), *Cedrus atlantica* (72 % at 9 mL/L) and *Foeniculum vulgaris* (76 % at 3 mL/L) [11,13,14], SI essential oil shows better inhibition performance. This result could be explained by the adsorption of phytochemical components of the essential oil 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.

In order to determine the components responsible for corrosion activity of the essential oil of *S. inaequidens*, firstly, we have studied separately the behavior of oxygenated fraction (OF) and hydrocarbon fraction (HF) obtained by the oil CC-chromatography. The results are summarized in Table 3.

Table 3. Gravimetric results of mild steel in 1 M HCl without and with addition of HF and OF fractions of *S. inaequidens* (*t*= 6h, *T*= 298 K).

Inhibitors	C (g/L)	W (mg/h.cm^2)	E_w (%)
	HCl 1 M	0.381	--
HF	0.25	0.168	**55.87**
	0.5	0.132	**65.41**
	1	0.102	**73.12**
	1.5	0.083	**78.25**
	2	0.067	**82.55**
OF	0.25	0.167	**63.72**
	0.5	0.106	**72.94**
	1	0.071	**75.17**
	1.5	0.052	**81.38**
	2	0.040	**86.54**

The results reveal that the inhibition efficiency Ew (%) increases with the concentrations of two fractions. Indeed, the OF fraction exhibited the maximum inhibition efficiency with 86.54 % at 2 g/L whereas the inhibition efficiency of HF fraction was 82.54 % at 2 g/L. The OF fraction was the most potent inhibitor of corrosion suggesting that the anticorrosive activity of this fraction is due to more polar constituents. Thus, we performed fractionation of OF in sub-fractions OF1 (Cacalohastine-rich fraction: 99.7 %).

In order to ensure the importance of the Cacalohastine **59**, we have realized its effectiveness against corrosion of steel in 1 M HCl. The values of percentage inhibition efficiency E_w (%) and

corrosion rate (W) obtained from weight loss method in 1 M HCl without and with different concentrations of Cacalohastine **59** at 298 K are summarized in Table 4.

Table 4. Weight loss results of mild steel in 1 M HCl without and with different concentrations of Cacalohastine **59** (*t*= 6h, *T*= 298 K).

Inhibitor	C (g/L)	W (mg/h.cm^2)	E_w (%)
Cacalohastine 59	0	0.381	--
	0.25	0.134	**64.82**
	0.5	0.083	**73.54**
	1	0.053	**78.17**
	1.5	0.036	**82.87**
	2	0.033	**87.17**

The results reveal that Cacalohastine **59** exhibited the maximum inhibition efficiency with 87.17 % at the concentration of 2 g/L. This indicated that the enhanced inhibitory activity of OF fraction observed under the same experimental condition might be due principally to Cacalohastine **59**. Moreover, the most inhibition of SI oil may be due to the adsorption, by a synergistic effect, of different phytochemical constituents present in two fractions (HF and OF).

In order to confirm the effectiveness of this essential oil, we made a depth study of the effect of temperature on the corrosion behaviour of mild steel in 1M HCl.

3.2.1. Effect of temperature and activation parameters $E°_a$, ΔS_a^o, $\Delta H°_a$

Generally, the corrosion rate of mild steel in acidic solution increase with the rise of temperature. This is due to the decrease of hydrogen evolution over potential [37]. In order to understand more about the performance of SI essential oil with the nature of adsorption and activation processes, the effect of temperature is studied with the range of temperature 303, 313, 323 and 333K for 1 h of immersion. The results are given in Table 5 and Fig 2.

Table 5. Corrosion parameters obtained from weight loss for mild steel in 1M HCl containing 2 g/L of *S. inaequidens* essential oil at different temperatures.

T (K)	W_{inh} mg/cm^2.h	W_0 mg/cm^2.h	E_w %
303	0.362	**4.178**	**91.33**
313	0.933	**7.419**	**87.43**
323	2.303	**11.178**	**79.40**
333	5.327	**17.369**	**69.33**
343	9.654	**19.369**	**50.16**

Inspection of these results 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 (E_w %) depends on the temperature and decreases with the rise

of temperature from 303 to 343 K. The decrease in inhibition efficiency with increase in temperature may be attributed to the increased desorption of inhibitor molecules from metal surface and the increase in the solubility of the protective film or the reaction products precipitated on the surface of the metal that might otherwise inhibit the reaction [38]. This is in accordance with the results reported by Ergun et al. [39].

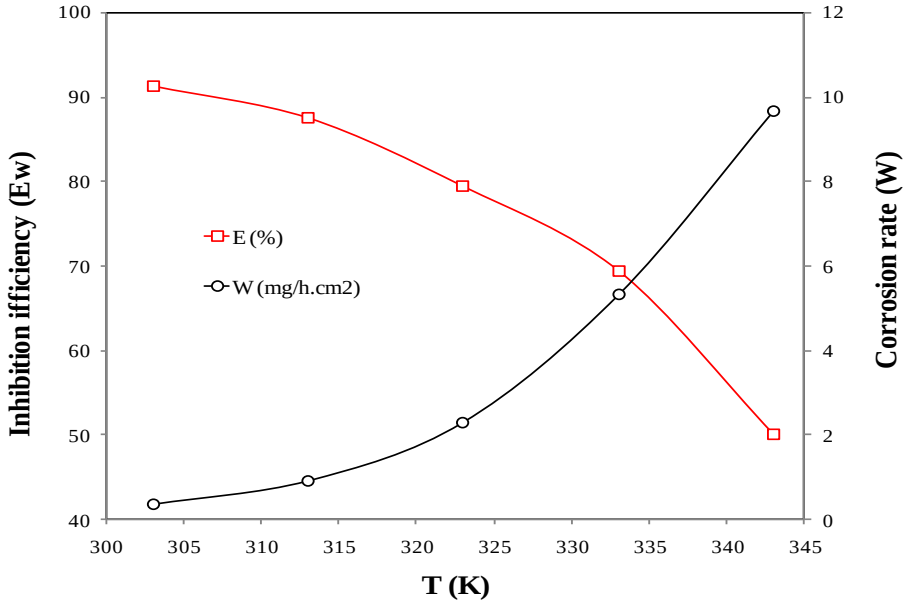


Figure 2. Variation of corrosion rate (W and inhibition efficiency (E_w) of corrosion of mild steel in 1 M HCl with different temperatures in the presence of *S. inaequidens* essential oil

In order to calculate activation thermodynamic parameters of the corrosion reaction such as activation energy E_a, activated entropy $\Delta S°_a$ and enthalpy $\Delta H°_a$, the Arrhenius equation and its alternative formulation called transition state equation were employed [28]. The logarithm of the corrosion rate of steel Ln W can be represented as straight-lines function of $10^3/T$ and the activation energy ($E°_a$) values were calculated from the Arrhenius plots (Fig. 3) and the results are shown in Table 7. Fig. 4 shows a plot of Ln (W/T) against $10^3/T$. Straight lines are obtained with a slope of ($-\Delta H°_a/R$) and an intercept of ($Ln(R/Nh) + (\Delta S°_a/R)$) from which the values of $\Delta H°_a$ and $\Delta S°_a$ are calculated and listed in Table 6.

Table 6. Activation parameters $E°_a$, ΔS_a^o, $\Delta H°_a$ of the dissolution of mild steel in 1 M HCl in the absence and presence of 2 g/L of *S. inaequidens* essential oil.

Inhibitor	$E°_a$ (KJ. mol^{-1})	$\Delta H°_a$ (KJ.mol^{-1})	$E-\Delta H°_a$ (KJ. mol^{-1})	$\Delta S°_a$ (J. mol-1.K^{-1})
HCl 1M	34.10	31.41	2.69	-128.86
+2 g/L SI essential oil	71.98	69.29	2.69	-24.62

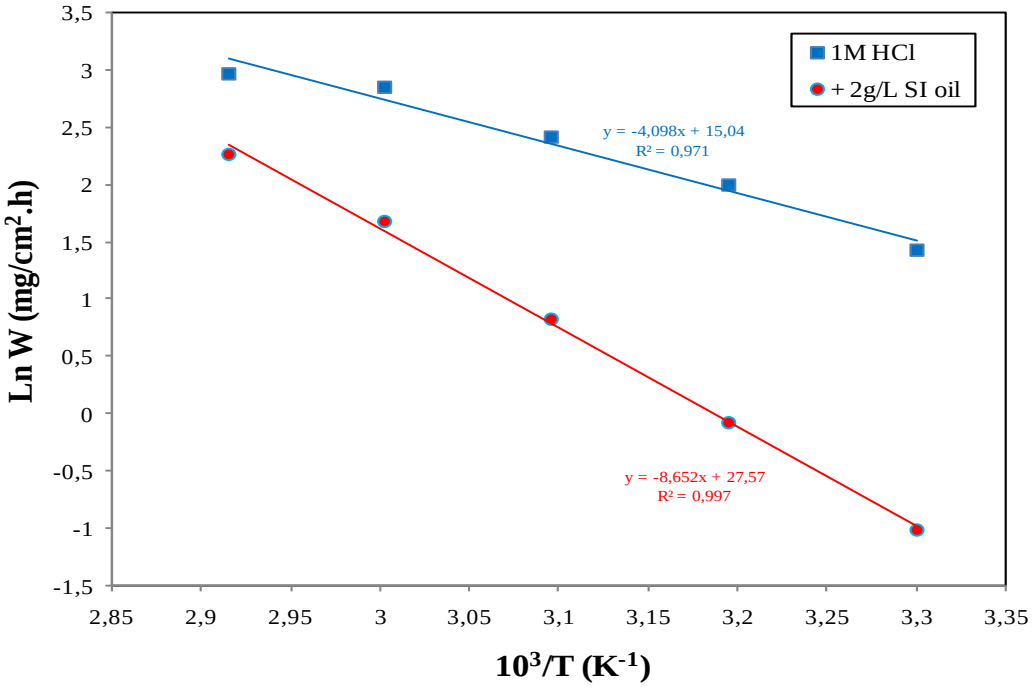


Figure 3. Arrhenius plots for mild steel corrosion rates (W) in 1 M HCl in absence and in presence of 2 g/L of *S. inaequidens* oil**.**

The calculated values of activation energies from the slopes are 34.10 and 71.98 kJ.mol^{-1} for free acid and with the addition of 2 g/L of SI essential oil, respectively. We remark that the activation energy increases in the presence of inhibitor. The higher $E°_a$ values, for inhibited solution than the uninhibited one, indicate that a strong inhibitive action of the additives by increasing energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on the mild steel surface [40]. In addition, the value of activation energy that is around 40–80 kJ.mol^{-1} can be suggested to obey the physical adsorption (physiosorption) mechanism [41].

Moreover, inspection of the data of Table 6 reveals that the positive signs of $\Delta H°_a$ both in the absence and presence of 2 g/L of SI essential oil reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow [42].

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 Eq. (5) of perfect gas [43]:

$$E°a - \Delta H°a = RT \qquad (5)$$

On the other hand, the entropy of activation ($\Delta S°_a$) 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 [44].

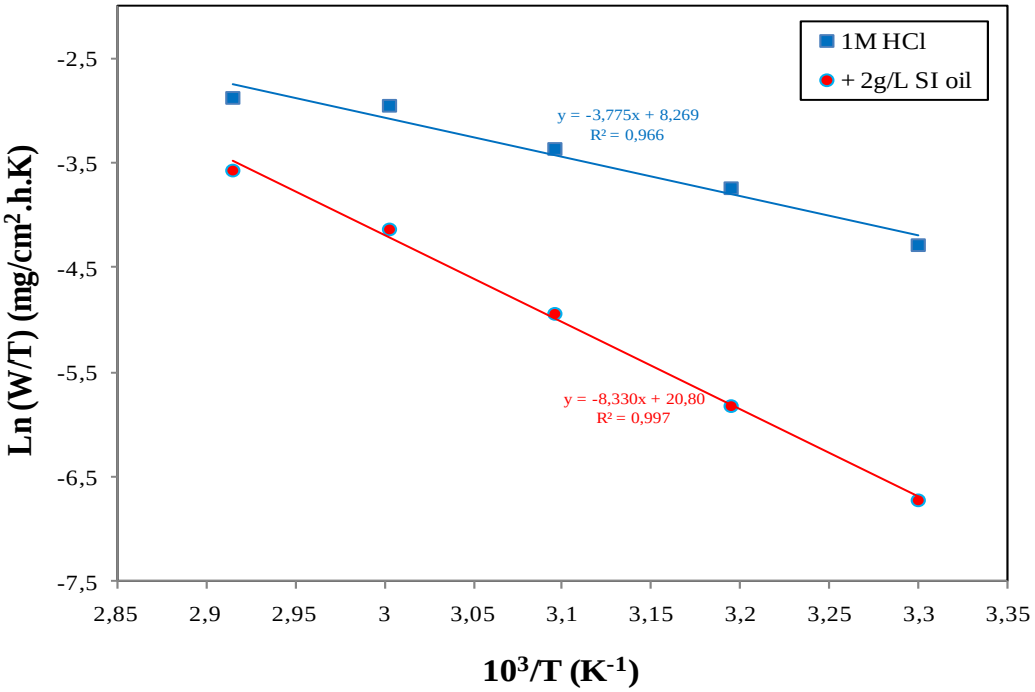


Figure 4. Transition-state plots for mild steel corrosion rates (W) in 1 M HCl in absence and in presence of 2 g/L of *S. inaequidens* essential oil.

3.3. Adsorption isotherm considerations

The adsorption process of inhibitor depends on the its electronic characteristics, the nature of metal surface, temperature, steric effects and the varying degrees of surface-site activity [45,46]. In fact, the solvent H_2O molecules could also be adsorbed at the metal/solution interface. Therefore, the adsorption of inhibitor molecules from the aqueous solution can be considered as a quasi-substitution process between the inhibitor in the aqueous phase $Inh_{(sol)}$ and water molecules at the electrode surface $H_2O_{(ads)}$ [47]:

$$Inh_{(sol)} + xH_2O_{(ads)} \leftrightarrow Inh_{(ads)} + xH_2 \qquad (6)$$

where x is the size ratio, that is, the number of water molecules re-placed by one organic inhibitor.

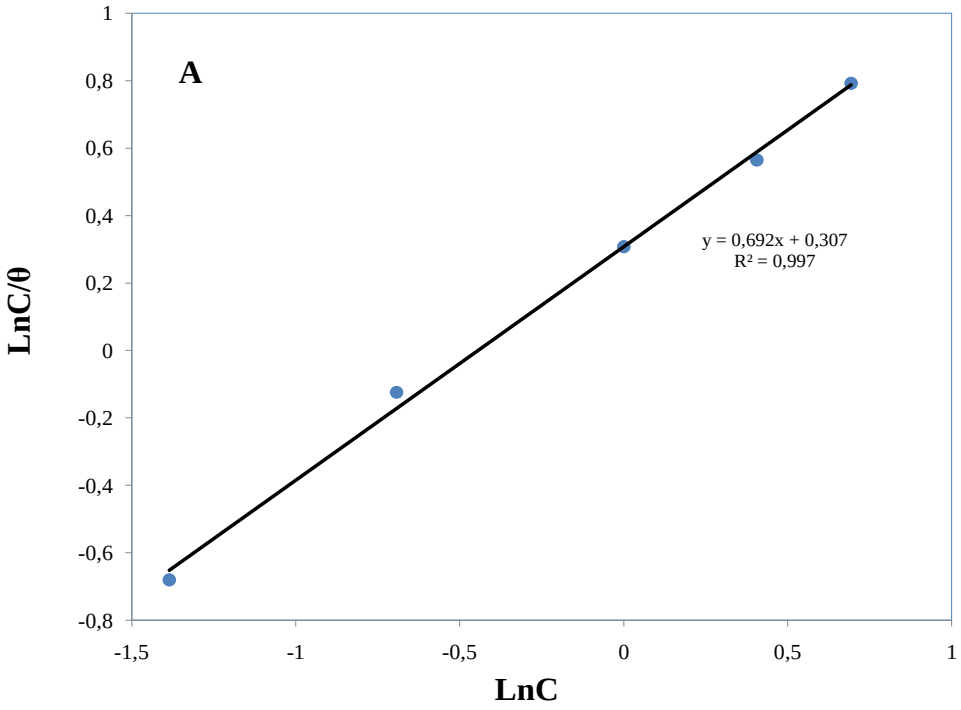
To obtain an effective adsorption of an inhibitor on metal surface, the interaction force between metal and inhibitor must be greater than the interaction force of metal and water molecule [48]. The corrosion adsorption processes can be understood using adsorption isotherm. Langmuir adsorption isotherm is attributing to physisorption or chemisorption phenomenon while Temkin adsorption isotherm gives an explanation about the heterogeneity formed on the metal surface. Chemisorption is attributed to Temkin isotherm [49]. Here, Langmuir, Frumkin and Temkin adsorption isotherms were applied in order to explain the adsorption process of SI essential oil on the mild steel surface:

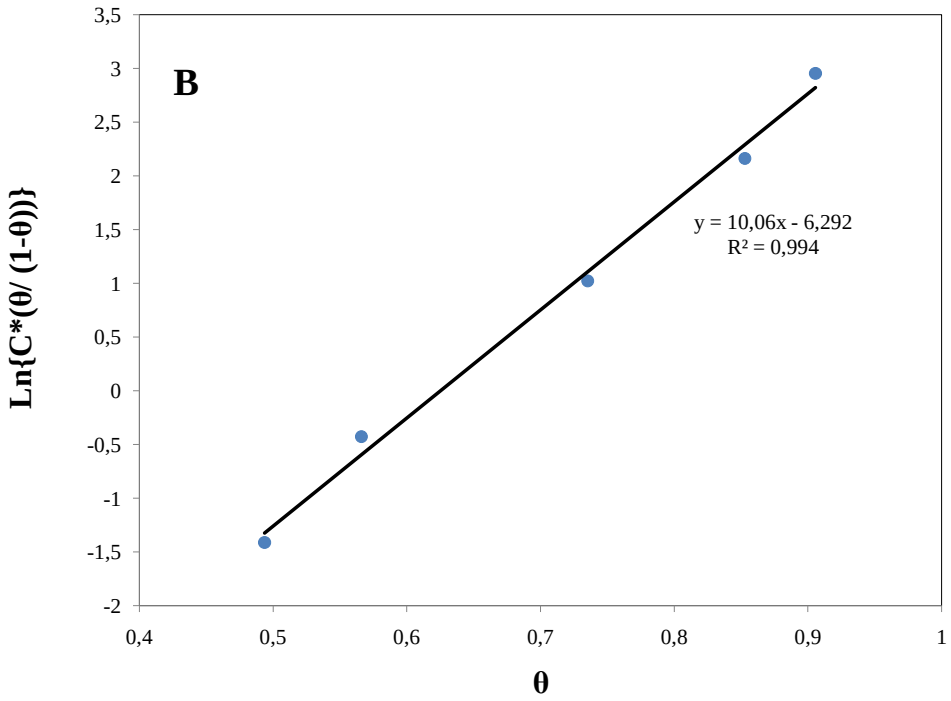
$$\text{Lamgmuir} : \frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \qquad (7)$$

$$\text{Temkin} : \text{Ln}\left(\frac{C_{inh}}{\theta}\right) = \text{LnK} - g\theta \qquad (8)$$

$$\text{Frumkin} : \text{Ln}\left(C_{inh} * (\frac{\theta}{1-\theta})\right) = \text{LnK} + g\theta \qquad (9)$$

where θ is the surface coverage, K is the adsorption–desorption equilibrium constant, C is the concentration of inhibitor and g is the adsorbate parameter.





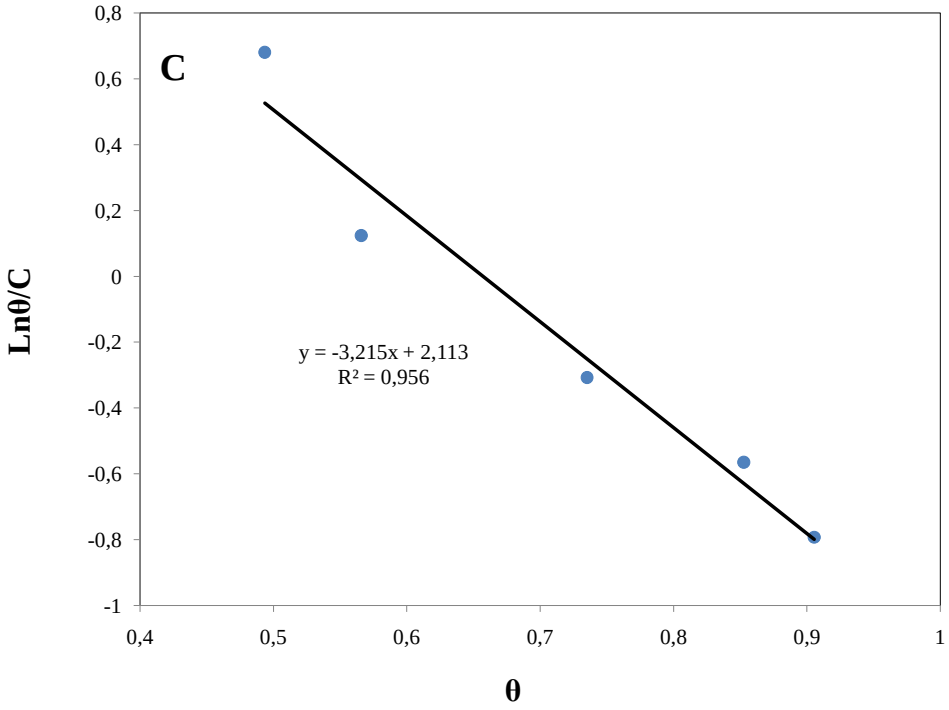


Figure 5. (A) Langmuir, (B) Frumkin and (C) Temkin isotherm for the adsorption of *S. inaequidens* essential oil on the surface of mild steel in 1 M HCl.

Again, the weight loss measurements were employed in this experiment with the concentration range 0.25 to 2g/L at 298 K. The corresponding plots are shown in Fig. 5, where the r^2 value for Langmuir isotherm (Fig. 5A) was 0.997, Frumkin isotherm (Fig. 5B) was 0.994 and Temkin isotherm (Fig. 5C) was 0.956. From this observation, it is concluded that Langmuir isotherm shows the best correlation with the experimental data. In addition, this also explains the monolayer formation of the inhibitor onto the mild steel surface [50, 51].

The free energy of adsorption $\Delta G°_{ads}$, also can be calculated using the following equation:

$$\Delta G°_{ads} = -RTLn(k * 55.5) \qquad (10)$$

where 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 (1000g/L).

The calculated value of free energy of adsorption was found to be $\Delta G°_{ads} = -16.366$ kJ.mol^{-1}, where adsorption–desorption equilibrium constant K value was obtained from the linear regression of Langmuir isotherm (K= 0.7 L/g). The negative value of $\Delta G°_{ads}$ indicates that the inhibitor, in this case SI essential oil is spontaneously adsorbed onto the mild steel surface. It is well known that values of $\Delta G°_{ads}$ around −20 kJ.mol^{-1} or lower are associated with the physiosorption phenomenon where the electrostatic interaction assemble between the charged molecule and the charged metal, while those around −40 kJ.mol^{-1} or higher are associated with the chemiosorption phenomenon where the sharing or transfer of organic molecules charge with the metal surface occurs [52, 53]. Hence, it is clear that SI essential oil is physically adsorbed onto the mild steel surface. Moreover, the decrease of inhibition efficiency with the increase in temperature may supports that the adsorption of SI essential oil on the

mild steel surface is physical in nature. As the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency.

3.4. Mechanism of inhibition

Accordingly, the effectiveness of inhibiting corrosion by an essential oil is closely related to its chemical composition which includes a non-polar, hydrophobic, consisting of hydrocarbon molecules and a polar, hydrophilic, which presents one or more functional groups [54]. Indeed, the inhibitive action of *S. inaequidens* essential oil could be attributed to the adsorption of its components on the mild steel surface by a synergistic action of oxygenated and hydrocarbon terpenes, especially their major constituents (Fig. 6). Thus, the inhibition efficiency of hydrocarbon terpenes could be attributed to the presence of a hydrophobic film in contact with the metal surface, which is constant and that somehow contribute to the interaction between the compounds or corrosive species and metal [55,56]. Also, the inhibition efficiency of oxygenated terpenes could be attributed to the presence of Oxygen atoms in functional groups (O–H, C=O, C–O,) and π-electrons of the aromatic ring or the double bonds in their structure, which meets the general characteristics of typical corrosion inhibitors which.

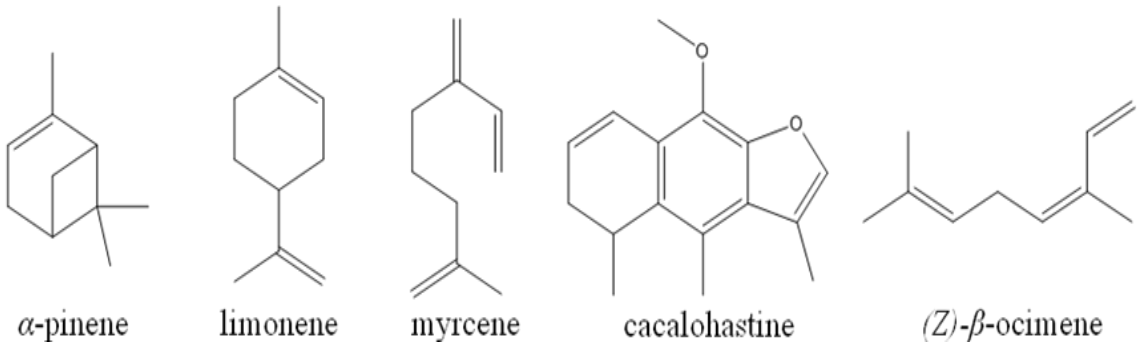


Figure 6. Structure of main components of *S. inaequidens* essential oil.

Generally, the inhibition of SI essential oil may be due to the adsorption of phytochemical constituents present in the oil by one and/or more of the following ways [57-59]:

(1) presence of a hydrophobic film, in contact with the metal surface, by the adsorption of hydrocarbon tepenes ;

(2) electrostatic interaction of protonated molecules with already adsorbed chloride anions (Cl);

(2) donor-acceptor interactions between the π-electrons of aromatic ring and vacant d orbital of surface iron atoms;

(3) interaction between unshared electron pairs of oxygen atoms and vacant d-orbital of iron surface atoms.

4. CONCLUSION

The study of chemical composition and effect of *Senecio inaequidens* essential oil on the corrosion of mild steel in 1 M HCl conducted by weight loss measurements may draw the following conclusions:

(1) Chemical analysis shows that myrcene (21.4 %), *(Z)-β*-ocimene (17.6 %), *α*-pinene (12.5 %), limonene (8.1 %) and cacalohastine (6.8 %) were the most abundant components of *S. inaequidens* essential oil from Corsica;

(2) Inhibition efficiency increases with the concentration of inhibitor and decreases with temperature;

(3) *Senecio inaequidens* essential oil acts as good inhibitor for the corrosion of mild steel in 1 M HCl with inhibition efficiency 90.56 % at 2g/L;

(5) Inhibition efficiency on mild steel may occur by synergistic action of hydrocarbons (87.5 %) and oxygenated terpenes (11.8 %).

References

1. G. Blustein, J. Rodriguez, R. Romanogli, C.F. Zinola, *Corros. Sci*. 47 (2005) 369.
2. O.K. Abiola, N.C. Oforka, E.E. Ebenso, N.M. Nwinuka, *Anti-Corr. Meth. Mater*. 54 (2007) 219.
3. N.O. Eddy, EE. Ebenso, *Afr. J. Pure Appl. Chem*. 2 (2008) 46.
4. S. Bilgic, *Korozyon* 13 (2005) 3.
5. G.O. Avwri, F.O. Igho, *Mater. Lett*. 7 (2003) 3705.
6. M. Znini, L. Majidi, A. Bouyanzer, J. Paolini, J.M. Desjobert, J. Costa, B. Hammouti, *Arab. J. Chem*. 5 (2012) 467.
7. A. Chetouani, B. Hammouti, M. Benkaddour, *Pig. Resin. Technol*. 33 (2004) 26.
8. A. El Bribri, M. Tabyaoui, B. Tabyaoui, H. El Attari, F. Bentiss, *Mater. Chem. Phys.* 141 (2013) 240.
9. M. Znini, J. Paolini, L. Majidi, J.-M. Desjobert, J. Costa, N. Lahhit, A. Bouyanzer, *Res. Chem. Intermed*. 38 (2012) 669.
10. A. Bouyanzer, B. Hammouti, L. Majidi, *Mater. let.* 60 (2006) 2840.
11. A. Bouyanzer, B. Hammouti, L. Majidi, *Mat. Lett*. 60 (2006) 2840.
12. A. Bouyanzer, L. Majidi, B. Hammouti, *Bull. Electrochem*. 22 (2006) 321.
13. O. Ouachikh, A. Bouyanzer, M. Bouklah, J-M. Desjobert, J. Costa. B. Hammouti, L. Majidi, *Surf. Rev. Lett*. 16 (2009) 49.
14. A. Bouyanzer, L. Majidi, B. Hammouti, *Phys. Chem. News*. 37 (2007) 70.
15. 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.
16. J. Gamisans. *Flora Corsica*, Edisud, 2004, pp. 797
17. D. Jeanmonod, *Complément au Podrome de la flore Corse, « Asteraceae II »*, Conservatoire botanique de Genève, (2004) pp 47-49.
18. Y. Yang, L. Zhao, Y. F. Wang, M. L. Chang C. H. Huo, Y. C. Gu, Q. W. Shi, H. Kiyota. *Chem. Biodiv.* 8 (2011) 13.
19. F. Conforti, R.M. Loizzo, A. Statti. Giancardo, J. H. Peter, F. Menichini. *Int. J. Food. Sci. Nut.* 57 (2006) 1.
20. M. R. Loizzo, A. Statti. Giancardo. R. Tundis, F. Conforti, M. Bonesi, G. Autelitano. *Phytother. Res.*, 18 (2004), 777.

21. European Pharmacopoeia, "Council of Europe". Strasbourg, 3rd ed, (1997) 121.
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 Gaz Chromatography/Quadrupole Mass Spectroscopy. Allured Publishing: Carol Stream, (2004).
24. NIST (National Institute of Standards and Technology), Spectral Database for Organic Compounds, NIST WebBook. http://webbook.nist.gov/chemistry, (2008).
25. National Institute of Standards and Technology (NIST). PC version 1.7 of the NIST/EPA/NIH Mass Spectral Library, Perkin Elmer Corp, Norwalk, CT, (1999).
26. C. Bicchi, E. Liberto, M. Matteodo, B. Sgorbini, L. Mondello, B. A. Zellner, R. Costa, P. Rubiolo, *Flavour Fragr. J.* 23 (2008) 382.
27. S. Andreani, T. Barboni, J. M. Desjobert, J. Paolini, J. Costa, A. Muselli. *Flavour Frag. J.* 27 (2012) 227.
28. J.O.M. Bockris, B. Young, *J. Electrochem. Soc*. 138 (1999) 2237.
29. M. Bouklah, N. Benchat, A. Aouniti, B. Hammouti, M. Benkaddour, M. Lagrenée, H. Vezine, F. Bentiss, *Prog. Org. Coat*. 51 (2004) 118.
30. M. Miyazawa, Y. Kawauchi, Y. Utsumi, T. Takahashi. *J. Oleo Sci*. 59 (2010) 527
31. K. Hayashi, H. Nakamura, H. Mitsuhashi, *Phytochem.* 12 (1973) 2931.
32. M. Okuyama, K. Umeyama, S. Ohmuri, M. Yamasaki, M. Satake, *Chem pharm Bull.* 42 (1994) 2183.
33. F. Bohlmann, M. Bapuji, *Phytochem.* 21 (1982) 681.
34. .281S. Abdo, M. de Bernardi, G. Marinoni, G. Mellerio, S. Samaniego, G. Vidarit, P. V. Finzit, *Phytochem*, 31 (1992), 3937.
35. X.H. Li, S.D. Deng, H. Fu, *Prog. Org. Coat*. 67 (2010) 420.
36. B. Zerga, M. Sfaira, Z. Rais, M. Ebn Touhami, M. Taleb, B. Hammouti, B. Imelouane, A. Elbachiri, *Mater. Tech*. 97 (2009) 297.
37. A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci*. 45 (2003) 33.
38. E.E. Ebenso, Hailemichael Alemu, S.A. Umoren, I.B. Obot, *Int. J. Electrochem. Sci*. 3 (2008) 1325.
39. U. Ergun, D. Yuzer, K.C. Emergul, *Mater. Chem. Phy*.109 (2008) 492.
40. M.I. Awad, *J. Appl. Electrochem*. 36 (2006) 1163.
41. K.O. Orubite, N.C. Oforka, *Mater. Lett*. 58 (2004) 1772.
42. N.M. Guan, L. Xueming, L. Fei, *Mater. Chem. Phys*. 86 (2004) 59.
43. M.K. Gomma, M.H. Wahdan, *Mater. Chem. Phys*. 39 (1995) 209.
44. S. Samkarapapaavinasam, M.F. Ahmed, *J. Appl. Electrochem*. 22 (1992) 390.
45. A.A. El-Awady, B.A. Abd-El-Nabey, S.G. Aziz, *J. Electrochem. Soc*. 139 (1992) 2149.
46. J.O'M. Bockris, A.K.N. Reddy, Modern Electrochemistry, vol. 2, Plenum Publishing Corporation, New York, (1976).
47. X. Wang, H. Yang, F. Wang, *Corros. Sci*. 52 (2010) 1268.
48. V.S. Sastri, E. Ghali, M. Elboujdaini, Corrosion Prevention and Protection: Practical Solutions, JohnWiley & Sons Ltd., 2007, p. 84.
49. M.S. Morad, A.M. Kamal El-Dean, *Corros. Sci*. 48 (2006) 3409.
50. M. A. Quraishi, D. Jamal, *Mater. Chem. Phys.* 71 (2001) 202.
51. S. Cheng, S. Chen, T. Liu, X. Chang, Y. Yin, *Mater. Lett*. 61 (2007) 3279.
52. F.M. Donahue, K. Nobe, *J. Electrochem. Soc*. 112 (1965) 886.
53. E. Khamis, F. Bellucci, R.M. Latanision, E.S.H. El-r, *Corrosion* 47 (1991) 677.
54. A.V. Fokin, M.V. Pospelov, E.S. Churshukov, L.P. Maiko, A.Ya. Sergeikin, Yu.N. Shekhter, T.I. Belova. *Chem. Tech. Fuels Oils*., 22 (1986) 62.

55. M. Kedam, O.R. Mattos, H. Takenouti. *J. Electrochem. Soc*, 128 (1981) 257. K. Magne. *J. of Disp. Sci. and Tech.*, 27 (2006) 587.
56. M.M. Singh, A. Gupta. *Corrosion*, 56 (2000) 371.
57. F. Bentiss, M. Traisnel, M. Lagrenée, *Corros. Sci*. 42 (2000) 127.
58. G.N. Mu, T.P. Zhao, M. Liu, T. Gu, *Corrosion*. 52 (1996) 853.
59. I. Ahamad, S. Khan, K.R. Ansari, M.A. Quraishi, *J. Chem. Pharm. Res*. 3 (2011) 703.