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Helichrysum italicum subsp. *italicum* Essential Oil as Environmentally Friendly Inhibitor on the Corrosion of Mil Steel in Hydrochloric Acid

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Essential oil of aerial parts of *Helichrysum italicum* subsp. *italicum* was obtained by hydrodistillation and analyzed by GC and GC/MS. 54 compounds accounting for 97.1 % of the oil were identified. This essential oil was characterized by having a high content of oxygenated monoterpenes (45.9%) with neryl acetate was a major compound (31.0%). The essential oil was also chromatographed by an automatized flash chromatography system. The inhibition of the corrosion of mild steel in Hydrochloric acid solution by HI essential oil and its various fractions have been studied using weight loss measurements. Inhibition was found to increase with increasing concentration of the essential oil to attain 82.33 % at 2g/L. The effect of temperature on the corrosion behavior of mild steel in 1M HCl without and with the HI 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 HI essential oil could serve as an environmentally friendly inhibitor of the corrosion of mild steel in Hydrochloric acid media.

Keywords: Adsorption, Corrosion Inhibition, Essential oil, Mild steel, *Helichrysum italicum* subsp. *italicum*.

1. INTRODUCTION

Hydrochloric acid is generally used as “pickling acids” for steel. Its function is to remove undesirable oxide coatings and corrosion products. Corrosion inhibitors used in acid treatment solutions significantly reduce the overall and local pickling attack and the hydrogen adsorption of steel strips [1]. Because of the general aggressively of acid solutions, corrosion inhibitors are commonly used to reduce the corrosive attack on metallic materials. There are various organic inhibitors which tend to decrease the corrosion rate of steel and iron in acidic solutions [2,3]. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions with S, O or N atoms in the molecule, heterocyclic compounds and π electrons. The polar function is usually regarded as the reaction centre for the establishment of the adsorption process [4]. Nevertheless, the known hazardous effects of most synthetic organic inhibitors and the need to develop non-toxic and environmentally benign processes have now made researchers to focus on the use of natural products.

Recently, the exploration of components of essential oils from various plant origins as inexpensive eco-friendly corrosion inhibitors is a innovative field of study. In addition to being environmentally friendly and ecologically acceptable, essential oils products are low-cost, readily available and renewable sources of materials [5]. The inhibition performance of essential oils is normally ascribed to the presence in their composition of complex organic species including oxygenated monoterpens and sesquiterpens as well as hydrcarbons products. These organic compounds usually contain polar functions with oxygen atoms as well as those with conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers.

In our laboratory, much work has been conducted to study the inhibition by essential oils on the corrosion of steel in acidic media. It has been reported that the essential oils of *Salvia aucheri* var. *mesatlantica* [6], *Mentha spicata* [7], *Warionia saharea* [8], *Lavandula multifida* [9], *Pulicaria mauritanica* [10] and *Asteriscus graveolens* [11] have been found to be very efficient corrosion inhibitors for mild steel in acid media. In our continuous quest to explore more essential oils as corrosion inhibitors, the present study is on *Helichrysum italicum* subsp. *italicum*.

The genus *Helichrysum* (family *Asteraceae*) from the tribe *Inuleae* comprises more than 400 species widespread throughout the world [12]. An overview of the numerous works relative to the genus *Helichrysum* points out a high degree of polymorphism [13] and suggests some pharmacological applications [14]. Several studies have been reported on the chemical composition of essential oils [15,16] and solvent extracts [17] of *Helichrysum* species from various origins.

Helichrysum italicum (Roth) G. Don fil., a typically Mediterranean species, is an aromatic shrub (50-70 cm high) with yellow flowers (blossoming time, May-June) growing on dry cliffs and sandy soils [18]. *H. italicum* oil is widely used in perfume industry and aromatherapy for their flavouring properties and biological activities (anti-inflammatory, anti-bacterial, anti-oxidant). The essential oils of three *H. italicum* subspecies have been studied: subsp. *serotinum* [19], subsp. *microphyllum* [20, 21] and subsp. *italicum* [21, 22]. Several analyses of essential oils (subspecies not specified) have been also reported in literature [23]. The chemical composition of *H. italicum* essential oil showed chemical variability among geographic origins such as Greece [22-24], Croatia [25], France [26, 27] and Italy [27, 28].

The essential oil of *H. italicum* has an economic importance in Mediterranean areas particularly for Corsica Island, due to high amount of neryl acetate. As part of our previous investigations on the characterisation of *H. italicum* oil [26-28], we have the chemical variability of these oils according to the vegetation cycle. The chemical compositions appeared also to be dependent on the sampling locations. For instance, Corsican and Sardinian essentials oils were characterized by the predominance of oxygenated compounds (neryl esters, eudesm-5-en-11-ol, β-di-ketones) and the Tuscany oil by the predominance of hydrocarbons compounds (□-pinene,□-curcumene) [26-28].

The objective of the present work is to study the inhibitive action of *Helichrysum italicum* subsp. *italicum* essential oil and its various fractions as a green and naturally occurring substance on corrosion behavior of mild steel in 1M HCl solution using weight loss measurements. In this case, the effect of concentration and temperature on the inhibition efficiency has been examined. The thermodynamic parameters for activation and adsorption processes were calculated and discussed.

2. EXPERIMENTAL PART

2.1. Plant material

The aerial parts of *H. italicum* subsp. *italicum* were harvested in July 2011 (full bloom) in Corsica (France). Voucher specimens of plants from each location were deposited in the herbarium of University of Corsica, Corte, France.

2.2. Essential oil isolation

Fresh aerial parts of *H. italicum* subsp. *italicum* were hydro-distilled during five hours using a Clevenger type apparatus in accordance with the method recommended in the European Pharmacopoeia [29]. The yield of essential oil was 0.46%

2.3. Oil fractionation

The essential oil of *Helichrysum italicum* subsp. *italicum* (4g) was separated by an automatized flash chromatography (AFC) system (*TeledyneEIsco,* Lincoln) using normal-phase silica (40g, 15-40µ, 60Å). The apolar (A) and polar (P) fractions (were eluted with hexane and iPr$_2$O, respectively (Fig. 1). The sub-fractions (P1, P2, P3) were eluted with a mixture of iPr$_2$O/hexane of increasing polarity. The elution gradient % iPr$_2$O/hexane (time) were: 0% (5min); 2% (7min); 5% (7min) and 100% (5min).

2.4. GC analysis

GC analysis were carried out using a Perkin-ElmerAutosystem XL GC apparatus equipped with dual flame ionization detection (FID) system and fused-silica capillary columns (60 m×0.22 mmI.D., film thickness 0.25 µm), Rtx-1 (polydimethylsiloxane) and Rtx-wax (polyethyleneglycol). The oven temperature was programmed from 60 °C to 230 °C at 2 °C/min and then held isothermally at 230 °C for 35 min. Injector and detector temperature was maintained at 280 °C. Samples were injected in the split mode (1/50), using helium as carrier gas (1 ml/min); the injection volume was0.2

µL of pure oil. Retention indices (RI) of compounds were determined relative to the retention times of series of *n*-alkanes (C_5-C_{30}) with linear interpolation, using the Van den Dool and Kratz equation [30] and software from Perkin-Elmer. Component relative concentrations were calculated based on GC peak areas without using correction factors.

2.5. GC-MS analysis

Samples were also analysed using a Perkin-Elmer Turbo mass detector (quadrupole), coupled to a Perkin-Elmer Autosystem XL, equipped with fused-silica capillary columns Rtx-1 and Rtx-Wax. Carrier gas: helium (1 mL/min), ion source temperature: 150 °C, oven temperature programmed from 60 °C to 230 °C at 2 °C/min and then held isothermally at 230 °C (35 min), injector temperature: 280 °C, energy ionization: 70 eV, electron ionization mass spectra were acquired over the mass range 35-350 Da, split: 1/80, injection volume: 0.2 µL of pure oil.

2.6. Identification of components

The methodology carried out for identification of individual components was based on (Table 1):

i) comparison of calculated retention indices (RI), on polar and apolar columns, with those of authentic compounds or literature data [31];

ii) computer matching with commercial mass spectral libraries [32] and comparison of mass spectra with those of our own library of authentic compounds or literature data [31,33].

2.7. Corrosion test

2.7.1. Preparation of materials

Mild steel coupons containing 0.09 wt.% (P), 0.38 wt.% (Si), 0.01 wt.% (Al), 0.05 wt.% (Mn), 0.21 wt.% (C), 0.05 wt.% (S) and the remainder iron (Fe) used for weight loss measurements. The surface preparation of the mild steel coupons (2 cm x 2 cm) was carried out with emery papers by increasing grades (400, 600 and 1200 grit size), then degreased with AR grade ethanol and dried at room temperature before use.

The aggressive solutions of 1.0 M HCl was prepared by dilution of analytical grade 37% HCl with double distilled water. The concentration range of the *H. italicum* subsp. *italicum* essential oil was 0.25-2 g/L. All reagents used for the study were of analytical grade

2.7.2. Weight loss measurements

Effect of concentration of inhibitors

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 presence of 2 g/L of different fractions and addition of different concentrations of *Helichrysum italicum* oil ranging from 0.25 to 2 g/L and fraction. 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:

$$W = \frac{\Delta m}{S.t} \qquad (1)$$

$$E_w\ \% = \frac{W_0 - W_{inh}}{W_0} \times 100 \qquad (2)$$

where Δm (mg) is the specimen weight before and after immersion in the tested solution, W_0 and W_{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).

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 [34]. The change of the corrosion rate with the temperature was studied in 1M HCl during 1 h of immersion, both in the absence and presence of inhibitor 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 [35]:

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

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S^{\circ}_a}{R}\right) \exp\left(-\frac{\Delta H^{\circ}_a}{RT}\right) \qquad (4)$$

where Ea 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 is the entropy of activation and ΔH°_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

The identification of essential oil components of *Helichrysum italicum* subsp. *italicum* was first carried out by using GC and GC/MS. Thus, 54 components were identified in the essential oil by comparison of their EI-MS and their retention indices (RI) with those of our own authentic compound library (Table 1).

Table 1. Essential oil composition of *Helichrysum italicum* subsp. *italicum*

n°[a]	Components	RIl[b]	RIa[c]	RIp[d]	%[e]	Identification[f]
1	2-Methyl-pentan-3-one	-	729	999	0.1	RI/MS
2	4-Methylhexane-3-one	-	799	1073	0.3	RI/MS
3	α-Pinene	936	930	1025	1.8	RI/MS
4	α-Fenchene	941	941	1060	0.5	RI/MS
5	Camphene	950	960	1069	0.1	RI/MS
6	β-Pinene	978	970	1111	0.8	RI/MS
7	Myrcene	987	980	1158	0.2	RI/MS
8	α-Terpinene	1013	1009	1178	0.2	RI/MS
9	ρ-Cymene	1015	1012	1266	0.3	RI/MS
10	Limonene*	1025	1022	1201	4.6	RI/MS
11	1,8-Cineole*	1024	1022	1209	0.7	RI/MS
12	trans-β-Ocimene	1041	1036	1246	0.2	RI/MS
13	γ-Terpinene	1051	1048	1242	0.5	RI/MS
14	2,4-Dimethylheptan-3,5-dione	-	1067	1515	0.3	RI/MS
15	Nonan-2-one	1074	1069	1381	0.4	RI/MS
16	Terpinolene	1082	1078	1279	0.2	RI/MS
17	Linalol	1086	1084	1537	2.7	RI/MS
18	Nerol oxide	1137	1135	1461	0.5	RI/MS
19	4,6-Dimethylheptan-3,5-dione	-	1159	1589	1.5	RI/MS
20	Terpinen-4-ol	1164	1161	1579	0.6	RI/MS
21	α-Terpineol	1176	1172	1707	0.5	RI/MS
22	Nerol	1210	1211	1787	4.0	RI/MS
23	Neral	1215	1213	1676	0.3	RI/MS

24	Geraniol	1235	1234	1863	0.2	RI/MS
25	Undecan-2-one	1273	1272	1579	0.2	RI/MS
26	Neryl acetate	1342	1349	1721	31.0	RI/MS
27	Geranyl acetate	1362	1360	1724	0.1	RI/MS
28	Isoitalicene	-	1375	1494	0.8	RI/MS
29	Italicene	1408	1402	1537	3.0	RI/MS
30	Cis-α-Bergamotene	1408	1409	1562	0.5	RI/MS
31	4,6,9-Trimethyldec-8-en-3,5-dione	-	1416	1875	4.6	RI/MS
32	Neryl propionate	1451	1434	1779	5.1	RI/MS
33	trans-α-Bergamotene	1434	1434	1578	0.3	RI/MS
34	(*E*)-α-Farnesene	1446	1446	1663	0.3	RI/MS
35	2,4,6,9-Tetramethyldec-8-en-3,5-dione#	-	1463	1879	4.5	RI/MS
36	2,4,6,9-Tetramethyldec-8-en-3,5-dione#	-	1475	1889		RI/MS
37	γ-Curcumene*	1473	1475	1686	10.7	RI/MS
38	α-Curcumene*	1475	1475	1764	3.5	RI/MS
39	Zingiberene	1485	1484	1722	0.4	RI/MS
40	5,7,10-Trimethylundec-9-en-4,6-dione	-	1495	1889	0.4	RI/MS
41	β-Curcumene	1503	1501	1733	0.7	RI/MS
42	(*E*)-α-Bisabolene	1530	1531	1764	0.2	RI/MS
43	(*E*)-Nerolidol	1553	1545	2024	0.4	RI/MS
44	3,5,7,10-Tetramethylundec-9-en-4,6-dione#	-	1555	1961	1.9	RI/MS
45	3,5,7,10-Tetramethylundec-9-en-4,6-dione#	-	1560	1961		RI/MS
46	Neryl isovalerate	-	1564	1870	0.4	RI/MS
47	Guaiol	1593	1584	2071	1.1	RI/MS
48	Eudesm-5-en-11-ol	-	1594	2102	2.3	RI/MS
49	5-Guaien-11-ol	1619	1602	2079	0.3	RI/MS
50	10-epi-γ-Eudesmol	1609	1604	2080	0.2	RI/MS
51	β-Eudesmol	1641	1618	2143	1.3	RI/MS
52	α-Eudesmol	1653	1632	2197	0.9	RI/MS
53	Bulnesol	1665	1649	2183	0.4	RI/MS
54	α-Bisabolol	1673	1663	2217	0.1	RI/MS
	Total identified				97.1	
	Monoterpene hydrocarbons				9.4	
	Sesquiterpene hydrocarbons				20.6	
	Oxygenated monoterpene				45.9	
	Oxygenated sesquiterpenes				6.8	
	Others				14.4	

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

b: RIl, Rentention indices on the apolar column, from [X].

c: RIa, Retention indices on the apolar column (Rtx-1).

d: RIp, Retention indices on the polar column (Rtx-Wax).
e: Percentage composition is given on the apolar column (percentages are given on the polar column for components marked with *).
f: RI: retention indices; MS: mass spectra in electron impact mode
: diastereoisomers

The oil was dominated by oxygenated monoterpenes (45.9%), neryl acetate being a major compound (31.0%). The essential oil of *Helichrysum italicum* subsp. *Italicum* (4 g) was first chromatographed by an automatized flash chromatography system (Figure 1). The fractionation led one apolar fraction A (1205 mg) and one polar fraction P (2795 mg). The polar fraction was further chromatographed leading three polar sub-fractions P1, P2, and P3. All fractions were also analysed by using GC and GC/MS. The main components of each fraction, their percentages and their number (corresponding to the order of elution on apolar column) are reported in Figure 1. The apolar fraction A was dominated by γ-curcumene C37 (60.9%), italicene C29 (18.6%) and isoitalicene C28 (4.3%). The polar fraction B exhibited neryl acetate C26 (46.6%), neryl propionate C34 (7.5%) and 2,4,6,9-tetramethyldec-8-en3,5-dione C35, C36 (6.0%) as major components. The sub-fraction P1 was characterized by a high amount of ester monoterpenic components such as neryl acetate C26 (75.2%). The sub-fraction P2 was dominated by □-diketones compounds such as 2,4,6,9-tetramethyldec-8-en-3,5-dione C35, C36 (27.1%), 4,6,9-trimethyldec-8-en-3,5-dione C31 (21.8%), 4,6-dimethyloctan-3,5-dione C19 (8.5%) and 3,5,7,10-tetramethylundec-9-en-4,6-dione C44+C45 (4.5%). Finally, the sub-fraction P3 was characterized by high content of alcohol terpenic compounds like nerol C22 (30.3%), eudesmol-5-en-11-ol C48 (11.3%), linalol C17 (8.2%), β-eudesmol C51 (7.0%) and α-eudesmol C52 (5.9%).

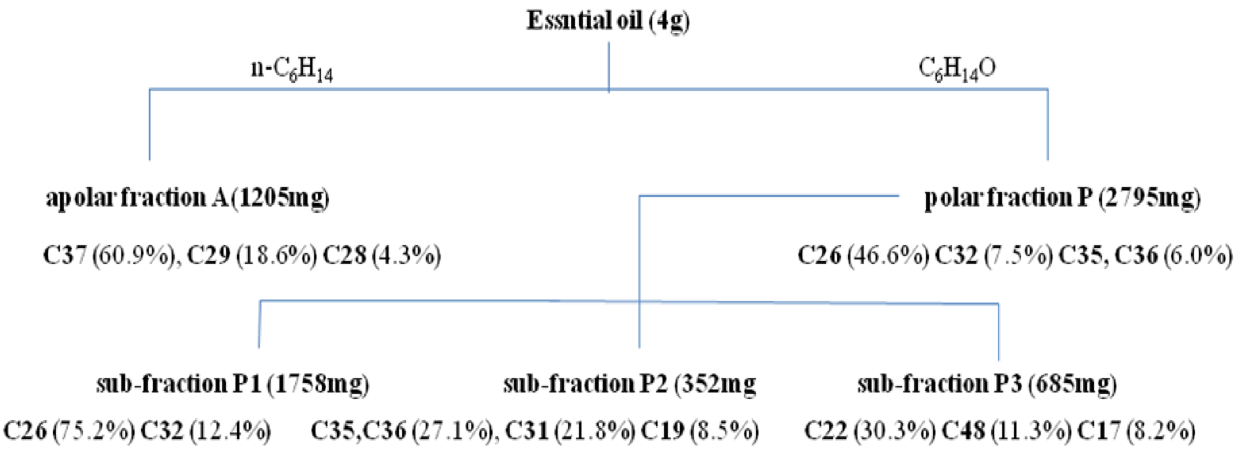

Figure 1. Fractionation of aerial parts essential oil of *Helichrysum italicum* subsp. *italicum*

3.2. Corrosion tests

3.2.1. Effect of Inhibitor Concentrations

The values of percentage inhibition efficiency Ew (%) and corrosion rate (W) obtained from weight loss method at different concentrations of *Helichrysum italicum* oil and its fractions at 298 K are summarized in Table 2.

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

Inhibitor	Concentration (g/L)	W (mg/h.cm^2)	Ew (%)
	0	0.381	--
Fraction A	2	0.159	58.4
Fraction P	2	0.120	68.4
Sub-fraction P1	2	0.127	66.8
Sub-fraction P2	2	0.079	79.3
Sub-fraction P3	2	0.076	80.1
	0.25	0.230	39.5
	0.5	0.160	58.0
Helichrysum italicum oil	1	0.082	78.4
	1.5	0.070	81.7
	2	0.067	82.3

The results reveal that the essential oil of *Helichrysum italicum* oil exhibited the maximum inhibition efficiency with 82.33 % at the concentration of 2 g/L whereas Sub-fraction P3, Sub-fraction P2, Fraction P, Sub-fraction P1 and Fraction A showed inhibition efficiencies with 80.14, 79.32, 68.44, 66.78 and 58.39 respectively at the concentration of 2 g/L. This indicated that the enhanced inhibitory activity of *Helichrysum italicum* oil observed under the same experimental condition might be due principally to alcohol terpenic compound (sub-fraction P3) and a low synergistic effect of phytochemicals present in the different fractions. In order to confirm the effectiveness of this essential oil, we made a depth study of the effect of *Helichrysum italicum* oil concentrations and temperature on the corrosion behavior of mild steel in1M HCl.

Ended, Table 2 and Fig. 2 shows that the corrosion rate (W) decreases noticeably with the inhibitor concentration from 0.381 to 0.067 mg cm^{-2} h^{-1} at 0 and 2 g/L of *Helichrysum italicum* oil, respectively, i.e. the corrosion of steel is retarded by *Helichrysum italicum* oil, or the inhibition enhances with the inhibitor concentration. This behavior is due to the fact that the adsorption coverage of inhibitor on steel surface increases with the inhibitor concentration [36]. It is clear also that the inhibition efficiency Ew (%) increases with the inhibitor concentration indicating that the extent of inhibition is dependent on the amount of *Helichrysum italicum* oil (concentration-dependent). Noticeably, when the concentration of *Helichrysum italicum* oil is less than 1.5 g/L, Ew increases sharply with an increase in concentration, but a further raise inhibitor concentration causes no appreciable change in inhibitive performance. At the inhibitor concentration of 2 g/L, the maximum Ew is 82.33 %. This indicates that the phytochemical components of the *Helichrysum italicum* 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.

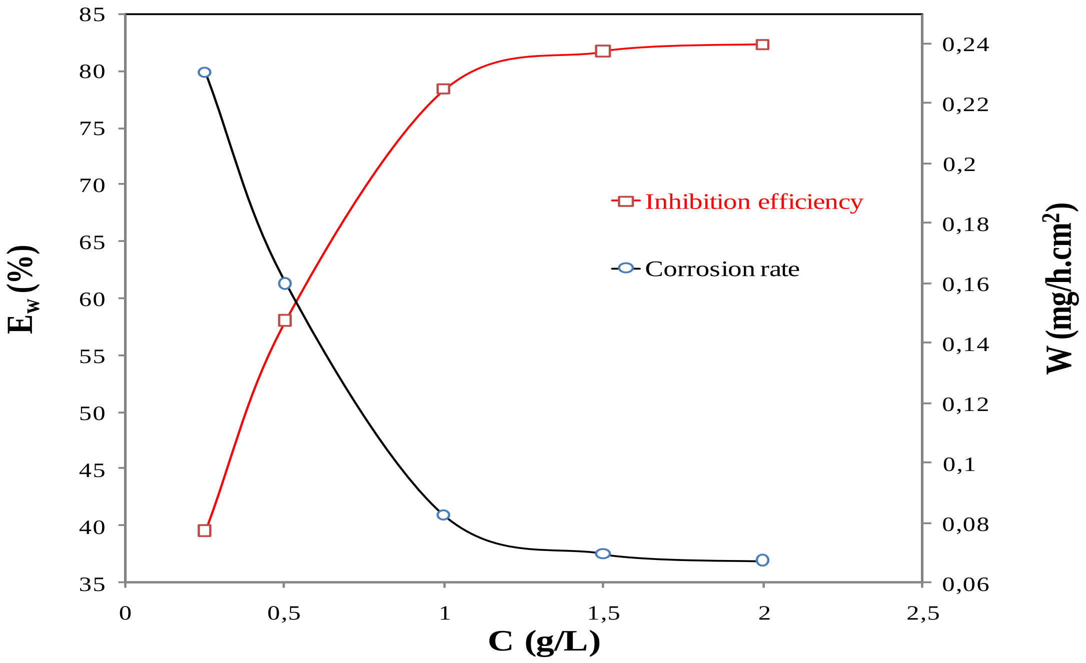

Figure 2. Variation of corrosion rate (W) and inhibition efficiency (Ew) of corrosion of mild steel in 1 M HCl with different concentration of *Helichrysum italicum* oil.

Similar view has been expressed on the inhibition of steel by essential oils in acidic solution. Ended and under similar conditions, Ew of *Mentha pulegium* oil is 80% at 2.76 g/L [37]. Therefore, comparing with some essential oils such as *Eucaliptus globulus* (72 % at 3 mL/L), *Cedrus atlantica* (72% at 9 mL/L) and *Foeniculum vulgari* (76 % at 3 mL/L) [38-40], *Helichrysum italicum* oil shows better inhibition performance. The results indicate that *Helichrysum italicum* oil is a good inhibitor for mid steel in 1M HCl solution.

3.2.1. Effect of temperature and activation parameters Ea, ΔSao, ΔH°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 [41]. In order to understand more about the performance of *Helichrysum italicum* 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 3 and Fig. 3.

Table 3. Corrosion parameters obtained from weight loss for mild steel in 1M HCl containing 2 g/L of *Helichrysum italicum* oil at different temperatures.

T (K)	Winh mg/cm^2.h	W0 mg/cm^2.h	Ew %
303	0.95	4.18	77.3
313	1.83	7.42	75.3
323	3.49	11.18	68.7
333	5.61	17.37	66.7
343	6.67	19.37	65.6

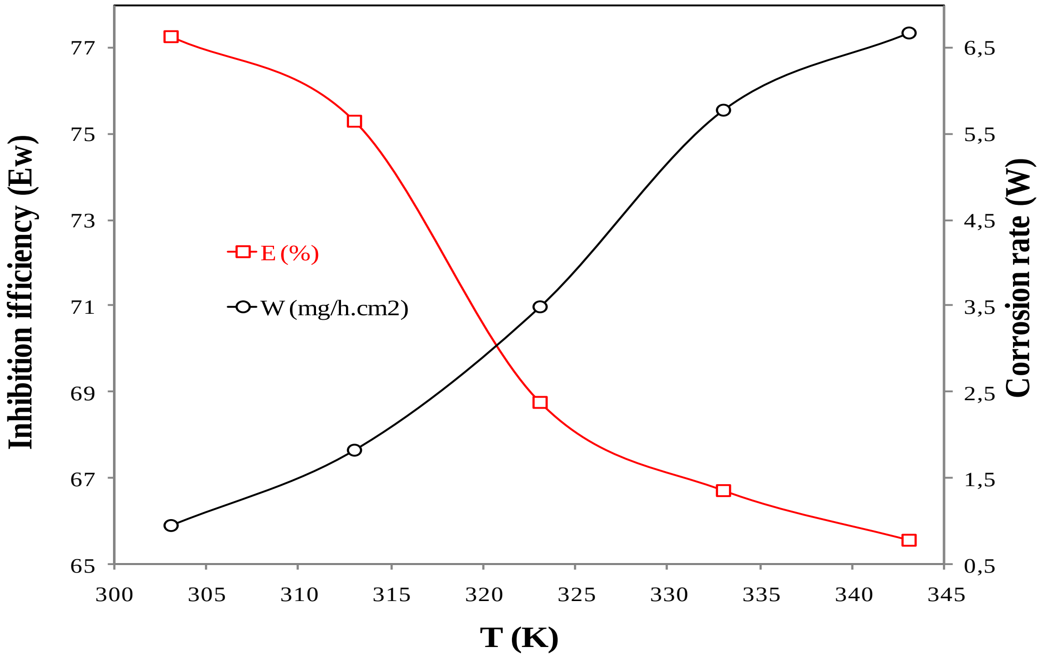

Figure 3. Variation of corrosion rate (W) and inhibition efficiency (Ew) of corrosion of mild steel in 1 M HCl with different temperatures in the presence of *Helichrysum italicum* oil.

Inspection of these results reveals that corrosion rate increases both in the uninhibited and inhibited acid solution with the rise of temperature especially goes up more rapidly in the absence of inhibitor. Also, we note that the efficiency (Ew %) 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 [42]. This is in accordance with the results reported by Ergun et al. [43].

In order to calculate activation 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 [34]. The activation corrosion energy (Ea) is calculated by linear regression between Ln W and 1/T (Fig. 4), and the result is shown in Table 4.

The logarithm of the corrosion rate of steel Ln W can be represented as straight-lines function of $10^3/T$ with the linear regression coefficient (R^2) was close to 1, indicating that the steel corrosion in hydrochloric acid can be elucidated using the kinetic model. The activation energy (E_a) values were calculated from the Arrhenius plots (Fig. 4) and the results are shown in Table 4. Fig. 5 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 4.

Table 4. Activation parameters E_a, ΔS_a^o, $\Delta H°_a$ of the dissolution of mild steel in 1M HCl in the absence and presence of 2 g/L of *Helichrysum italicum* 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 *Helichrysum italicum* oil	46.63	40.94	2.69	-109.74

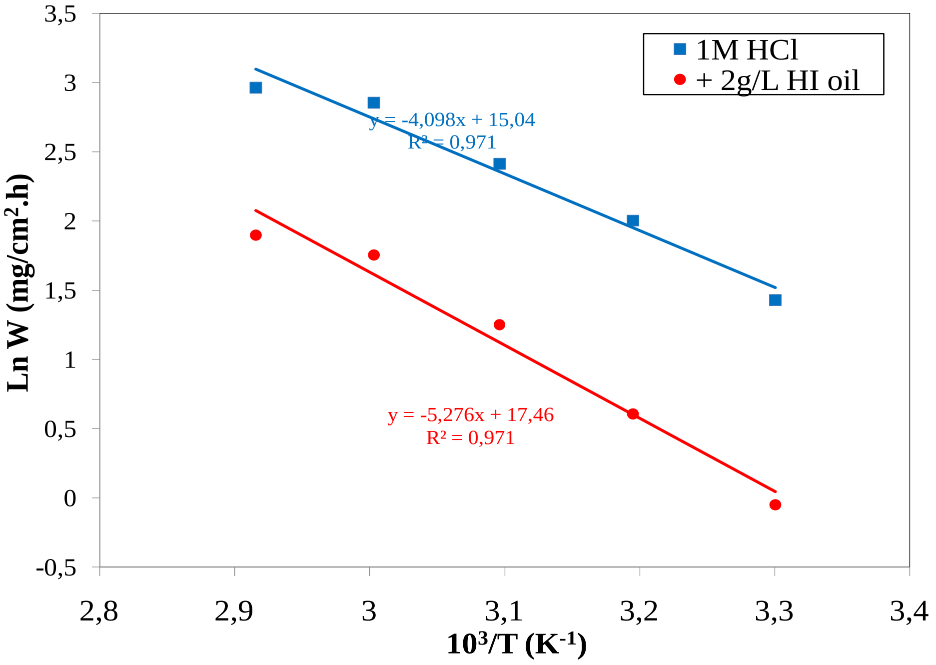

Figure 4. Arrhenius plots for mild steel corrosion rates (W) in 1M HCl in the absence and presence of 2 g/L of *Helichrysum italicum* oil (HI oil)**.**

The calculated values of activation energies from the slopes are 34.10 and 43.63 Kj/mol for free acid and with the addition of 2 g/L of *Helichrysum italicum* 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 [44]. According to Orubite et al. [45], the activation energy for physical adsorption mechanism should be less than 80kJ/mol. The higher Ea values in the presence of inhibitor compared to the blank solution indicates that the inhibitor will be effective at low temperatures, but efficiencies will be diminished at higher temperatures [46].

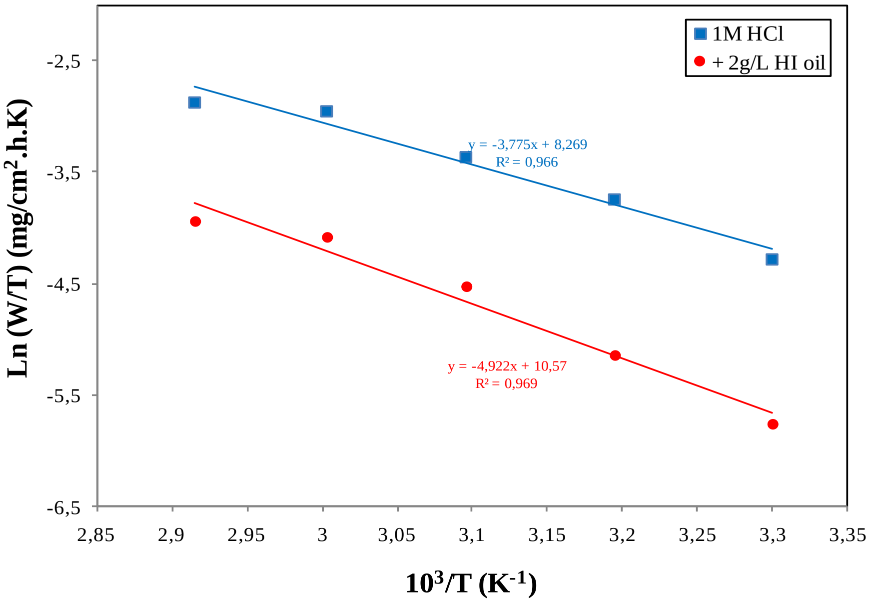

Figure 5. Transition-state plots for mild steel corrosion rates (W) in 1M HCl in absence and in presence of 2 g/L of *Helichrysum italicum* oil (HI oil).

Moreover, inspection of the data of Table 4 reveals that the positive signs of $\Delta H°_a$ both in the absence and presence of 2 g/L of *Helichrysum italicum* oil reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow [47]. Typically, enthalpy of physical adsorption process is lower than 80kJ/mol while the enthalpy of chemisorption process approaches 100 kJ/mol [48]. The value of the obtained enthalpy, therefore, suggests physical adsorption of the components of the *Helichrysum italicum* oil on the surface of the metal.

The average difference value of the E_a–$\Delta H°_a$ is 2.69 $kJmol^{-1}$, 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 [49]:

$$E_a - \Delta H_a^{\circ} = RT \qquad (5)$$

On the other hand, Large and negative values of entropies ($\Delta S°_a$) imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [50].

3.3. Adsorption isotherm considerations

Adsorption isotherms provide information about the interaction of the adsorbed molecules with the electrode surface [51,52]. The adsorption of organic adsorbate at the metal/solution interface can be presented as a substitution adsorption process between the organic molecules in aqueous solution ($Inh_{(sol)}$), and the water molecules on the metallic surface ($H_2O_{(ads)}$) [53].

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

where $Inh_{(sol)}$ and $Inh_{(ads)}$ are the inhibitor specie dissolved in the aqueous solution and adsorbed onto the metallic surface, respectively. $H_2O_{(ads)}$ is the water molecule adsorbed on the metallic surface and n is the size ratio representing the number of water molecules replaced by one organic adsorbate.

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 [54]. The corrosion adsorption processes can be understood using adsorption isotherm. The most frequently used adsorption isotherms are Langmuir, Temkin, and Frumkin. So these adsorption isotherms were tested for the description of adsorption behavior of *Helichrysum italicum* oil on steel surface in HCl solution. The correlation coefficient, R^2, was used to choose the isotherm that best fit experimental data. The fit to the Langmuir isotherm was determined by plotting C_{inh}/θ versus C_{inh} according to the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{b} + C_{inh} \qquad (7)$$

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

The θ values calculated using weight loss measurements at 298 K for steel in 1 M HCl with various concentrations of *Helichrysum italicum* oil. The corresponding plots are shown in Fig. 6. These plots are linear with a slope equal to unity. This behavior suggests that the compounds present in the *Helichrysum italicum* oil adsorbed onto the steel surface were consistent with a Langmuir adsorption isotherm, indicating that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species [55,56]. The free energy of adsorption $\Delta G°_{ads}$, also can be calculated using the following equation:

$$b = \frac{1}{55,5}.\exp\left(-\frac{\Delta G°_{ads}}{R.T}\right) \qquad (8)$$

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. The unit of b is L/g, which results in that the unit of c_{water} is g/L with the value of approximate 10^3.

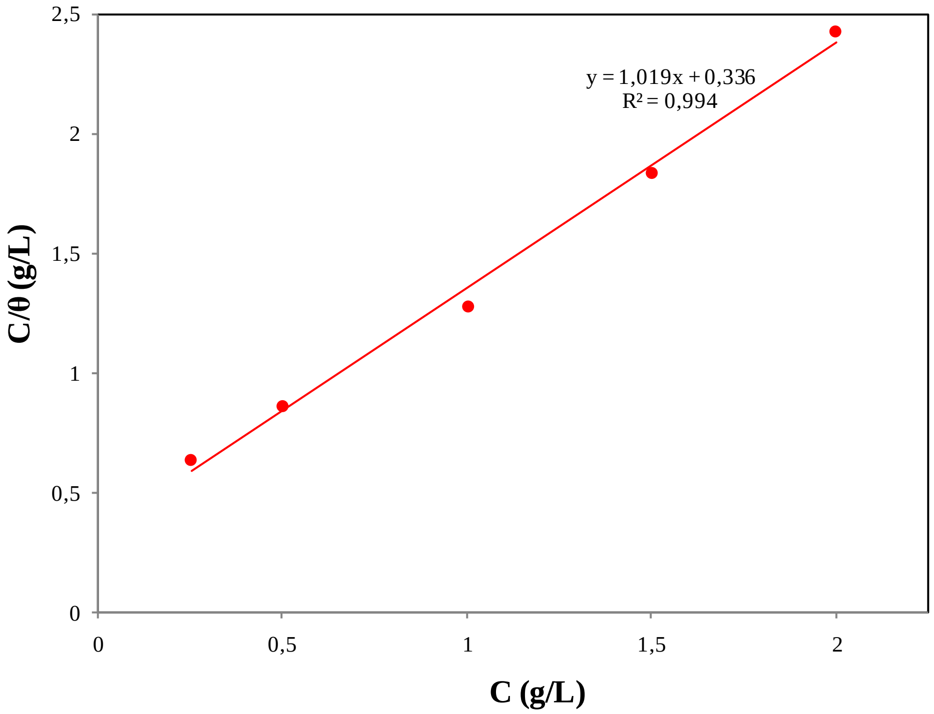

Figure 6. Variation of θ with different concentration of *Helichrysum italicum* oil on the surface of mild steel in 1M HCl fitted to langmuir isotherm.

3.4. Mechanism of inhibition

The *Helichrysum italicum* essential oil was dominated by oxygenated compounds (> 60 %). these compounds contain Oxygen atoms in functional groups (O–H, C=O, C–O,) and aromatic rings, which meets the general characteristics of typical corrosion inhibitors. Accordingly, the inhibitive action of *Helichrysum italicum* oil could be attributed to the adsorption of its components on the mild steel surface. Thus, it is reasonable to deduce that the oxygenated compounds in *Helichrysum italicum* oil exhibit the inhibition performance. In aqueous acidic solution, the organic molecules of *Helichrysum italicum* oil exist either as neutral molecules or in the form of protonated organic molecules (cation). Generally, two modes of adsorption are considered on the metal surface in acid media. 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 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 Cl^- have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favour 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 Cl^- ions and protonated inhibitors [57-59].

4. CONCLUSION

The study of chemical composition and effect of *Helichrysum italicum* subsp. *italicum* essential oil and its various fractions on the corrosion of mild steel in 1 M HCl conducted by weight loss measurements may draw the following conclusions:

- Chemical analysis shows that neryl acetate (31.0 %), γ-curcumene (10.7 %) and the two diastereosimers of 2,4,6,9-tetramethyldec-8-en-3,5-dione (4.7 %) were the major components of *H. italicum* subsp. *italicum* essential oil;

- *H. italicum* subsp. *italicum* essential oil acts as good inhibitor for the corrosion of mild steel in 1 M HCl with inhibition efficiency 82.33 % at 2g/L;

- Inhibition efficiency increases with the concentration of inhibitor and decreases with temperature;

- Inhibition efficiency of *H. italicum* subsp. *italicum* essential oil might be due principally to alcoholic terpenic compounds (sub-fraction P3).

- Inhibition efficiency on mild steel may occur by synergistic action of phytochemicals presents in *H. italicum* subsp. *italicum* essential oil.

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