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Chemical Composition and Anticorrosive Activity of *Warionia Saharea* Essential Oil Against the Corrosion of Mild Steel In 0.5 M H_2SO_4

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Essential oil of aerial parts of *Warionia saharea* was obtained by hydrodistillation and analyzed by GC and GC/MS. 39 compounds accounting for 93.2 ± 1.9% of the oil were identified. β-Eudesmol (34.9 %), Nerolidol-E (23%) and Linalool (15.2 %) were the most abundant components. The inhibition of the corrosion of mild steel in sulfuric acid solution by *Warionia saharea* essential oil has been studied using weight loss measurements. Inhibition was found to increase with increasing concentration of the essential oil to attain 74% at 3g/L. The effect of temperature, immersion time on the corrosion behaviour of mild steel in 0.5M H_2SO_4 without and with the *W. saharea* oil at 3 g/L was also studied. The associated activation energy has been determined. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. The adsorption of the molecules of the essential oil on the mild steel surface obeyed the Langmuir adsorption isotherm. The results obtained showed that the *Warionia saharea* essential oil could serve as an effective inhibitor of the corrosion of mild steel in sulfuric acid media.

Keywords: Corrosion, Inhibition, Hydrodistillation, Essential oil, *Warionia saharea*, mild steel.

1. INTRODUCTION

The importance of protection against corrosion in acidic solutions is increased by the fact that steel materials, which are more susceptible to be attacked in aggressive media, are the commonly exposed metals in industry especially for structural applications [1]. Sulphuric acid, for example, is often used as a pickling acid for mild steel to remove undesirable corrosion products. The chemical acid cleaning will cause metal corrosion upon the already cleaned surface after the elimination of the corrosion products [2]. The use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption [3]. However, they are not considered as long-term solutions due to the concerns associated with exposure risks health and environmental hazards residue persistence [3].

Recently, several studies have been carried out on the inhibition of corrosion of metals by plant extract especially essential oils. Thus, we previously reported that *Salvia aucheri mesatlantica* oil [4], *Mentha spicata* oil [5], *Mentha pulegium* oil [6], *Eucalyptus globulus oil* [7], *Simmondsia chinensis* oil [8], *Rosmarinus officinalis oil* [9-11], *Artemisia herba-alba* oil [12-14], *Lavendula dentata* oil [15], *Cedrus atlantica oil* [16] and *Foeniculum vulgaris* oil [17] have been found to be very efficient corrosion inhibitors for mild steel in acid media. As a contribution to the current interest on environmentally friendly, green, corrosion inhibitors, the present study investigates the inhibiting effect of *Warionia saharea* essential oil, as safe corrosion inhibitors for the mild steel corrosion in H_2SO_4 solutions.

The genus *Warionia* is a monotypic genus of *Asteraceae* endemic to the north-western edge of the African Sahara desert [18]. The species *W. saharae* is a somewhat thistle-like aromatic plant of 1 to 3 m of height, with white latex and fleshy, pinnately-partite leaves. The thick trunk is covered of a gray peel, structural of very wavy terminal leaf bouquets and of capitulate of yellow flowers. The flowering season has been recorded from April to June, while it may extend to July or August if the spring rains are abundant and well spaced [19,20].

In Morocco, *W. saharae* grows on slopes of the High Atlas, Anti-Atlas and Saharian Atlas in the coast of western Morocco and in desert areas on basic and siliceous rocks from 0 to 1300 m (Fig. 1). This plant, known locally by the vernacular name of “afessas”, is considered to have medicinal properties mainly by its essential oils [21]. Decoction of dried leaves is used as antirrheumatic, for gastrointestinal disorders and against epileptic crisis [22]. Crude extracts of the plants showed antibacterial and cytotoxic activities against a cancer cell line (KB cells) [23].

Figure 1. *Warionia saharea* Benth. & Coss, in its native habitat in south-eastern of Morocco

The aim of this study was to obtain for the first time information on the chemical composition of *W. saharea* essential oil and its inhibitory effect against the corrosion of mild steel in 0.5M H_2SO_4 using weight loss measurements.

2. MATERIAL AND METHODS

2.1. Plant material

The aerial part (leaves and flowers) of *Warionia sahare* were harvested in March/April 2009 from Morocco on seven localities: Mellab, Alnif, Assoul, Tata, Ouarzazate, Boudnib and Errachidia (center). Voucher specimens were deposited in the herbarium of biology unit, Faculty of Sciences and Technology of Errachidia (Marocco).

2.2. Essential oil isolation

The dried vegetal material (100 g) were water-distillated (3 h) using a Clevenger-type apparatus according to the method recommended in the European Pharmacopoeia [24] and the essential oils average yield was approx 1.20%.

2.3. GC analysis

GC analyses were carried out using a Perkin-Elmer Autosystem (Waltham, MA, USA) XL GC apparatus equipped with dual flame ionization detectors (FID) and fused-silica capillary columns (60 m x 0.22 mm i.d.; film thickness 0.25μm) coated with Rtx-1(polydimethylsiloxane) and Rtx-wax (polyethyleneglycol). The oven temperature was programmed from 60 to 230 °C at 2 °C/min and the held at 230 °C for 35 min. Injector and detector temperatures were maintained at 280 °C. Samples were injected in the split mode (1/50) using helium as carrier gas (1 mL/min); the injection volume of pure oil was 0.1 μL. Retention indices (RI) of compounds were determined relative to the retention times of series of n-alkanes (C5-C30), using the Van den Dool and Kratz equation [25].

2.4 GC-MS analysis

Samples were analysed with a Perkin-Elmer Turbo mass detector (quadrupole), coupled to Perkin-Elmer Autosystem XL chromatograph equipped with Rtx-1 and Rtx-wax fused-silica capillary columns. The carrier gas was helium (1mL/min), the ion source temperature was 150°C, the oven temperature was programmed from 60 to 230 °C at 2 °C/min and the held at 230 °C for 35 min, the injector was operated in the split (1/80) mode at a temperature of 280 °C, the injection volume was 0.2 μL of pure oil, theionization energy was 70 eV, EI/MS were acquired over the mass range 35-350 Da.

2.5. Components identification

The identification of the components was based on:

(1) a comparison between the calculated retention indices on the polar (Ir *p*) and apolar (Ir *a*) columns with those of pure standard authentic compounds and literature data [26,27];

(2) a comparison of the mass spectra with those of our own library of authentic compounds and with those of a commercial library [27,28].

2.6. Quantification of essential oil constituents

Quantification of the essential oil components was carried out using the methodology reported by Bicchi et al. [29], and modified as follows. The response factor (RF) of 29 standard compounds grouped into seven chemical groups (monoterpene hydrocarbons. sesquiterpene hydrocarbons. Alcohols, ketones, aldehydes, esters and others) was measured using GC (Table 1). RFs and calibration curves were determined by diluting each standard in hexane at five concentrations, containing tridecane (final concentration = 0.7 g/100 g) as an internal standard. Analysis of each standard was performed in triplicate. For the quantification of the essential oil components, tridecane (0.2 g/100 g) was added as internal standard to the essential oil. The correction factor (average of the response factors from standards) of each chemical group was calculated and used to determine the essential oil component concentration (g/100 g) according to the chemical group.

Table 1. Measurement of response factors (RFs) of the different chemical groups (SD: standard deviation).

Compounds	RF±SD	Compounds	RF±SD
Monoterpene hydrocarbons	1.01±0.05	(E)-2-Hexenal	1.39±0.01
neo-allo-Ocimene	1.00±0.01	(E,E)-2,4-Decadienal	1.42±0.01
α-Pinene	1.04±0.01	(E)-2-Decenal	1.40±0.01
β-Pinene	1.08±0.01	Ketones	1.30±0.02
γ-Terpinene	1.01±0.01	Artemisia ketone	1.30±0.01
Limonene	0.94±0.01	decan-2-one	1.28±0.03
Sesquiterpene hydrocarbons	1.00±0.03	Camphor	1.31±0.01
β-Caryophyllene	0.98±0.01	Jasmone	1.32±0.01
α-Humulene	1.01±0.01	Esters	1.55±0.03
Aromadendrene	1.03±0.01	Pentyl acetate	1.53±0.01
Aromatic hydrocarbon	0.93±0.04	Lavandulyl acetate	1.54±0.01
p-cymene	0.93±0.04	trans-Myrtenyl acetate	1.53±0.01
Alcohols	1.34±0.04	Cedryl acetate	1.59±0.01
Nerol	1.31±0.02	Others	
Lavandulol	1.32±0.02	Caryophyllene oxide	1.59±0.01
Cedrol	1.31±0.02	Isoborneol methyl ether	1.25±0.01
Globulol	1.34±0.02	1,8-cinéole	1,25±0,01
(E)-3-Hexen-1-ol	1.40±0.02	Carvacrol methyl ether	1.23±0.01
Aldehydes	1.40±0.02		

2.2. Corrosion test

The aggressive solution (0.5M H_2SO_4) was prepared by dilution of Analytical Grade 98% H_2SO_4 with double-distilled water. Prior to all measurements, the mild steel samples (0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron) were polished with different emery paper up to 1200 grade, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and drying at room temperature.

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 mL with and without the addition of different concentrations of inhibitor ranging from 0.25 g/L to 3 g/L. The mild steel specimens used had a rectangular form (2 cm x 2 cm x 0.05 cm). The immersion time for the weight loss was 6 h at 298 K. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in $mg.cm^{-2}\ h^{-1}$. The immersion time effect was studied in intervals of 2 to 8 h in the presence of 3 g/L of inhibitor at 298 K. The temperature effect on the corrosion behaviour of mild steel in 0.5M H_2SO_4 without and with the inhibitor at 3 g/L was studied in the temperature range from 303 and 343 K.

3. RESULTS AND DISCUSSION

3.1. Essential oil composition

The identification of essential oil components of *W. saharea* was carried out using GC and GC-MS according to the methodology described in experimental part. Thus, 39 components accounting for 93.2 ± 1.9% of the oils were identified by comparison of their EI-mass spectra and their retention indices with those of our own authentic compound library (Table 2).

The component concentrations (g/100g of essential oil) were determined using correction factors of each chemical group (averages of response factors RFs from standards) according to the methodology described by Bicchi et al. [29]. The seven locations from Morocco showed several similarities from a qualitative and quantitative viewpoint (Table 2). The chemical composition of the essential oils was dominated highly by the oxygenated sesquiterpenes (62.8%) followed by oxygenated monoterpenes (28%). The most abundant compounds were β-Eudesmol 36 (34.8%), Nerolidol-E 33 (23.6%) and Linalool 16 (15.4%). These three compounds represent 73.1% of the total oils (Fig. 2). These results were in accordance with those previously reported in literature [30,31]. Indeed, Ramaut et al. identified only 3 compounds such as eudesmol (42.25%), linalool (8.63%) and nerolidol (17.26%) [30]. Thirty compounds amounting 91% of the oil, were identified by Essaqui et al [31]. The major components were β-eudesmol (52.7%), trans-nerolidol (17.4%) and linalool (5.1%) [31].

Table 2. Chemical composition of essential oils from *W. saharea* collected on seven various stations in south-eastern of Morocco

N°[a]	**Components**	**Ir *l*[b]**	**Ir *a*[c]**	**Ir *p*[d]**	**Components concentration (g/100g)[e]**		
					Seven stations		
					Aerial parts		
					average ± SD	min	max
1	*α*-Thujene	932	921	1025	0.1 ± 0.0	-	0.1
2	*α*-Pinene	936	928	1025	0.1 ± 0.1	-	0.3
3	Camphene	950	941	1060	0.3 ± 0.3	-	0.5
4	Sabinene	973	961	1114	0.1 ± 0.1	0.1	0.4
5	*β*-Pinene	978	966	1104	0.1 ± 0.1	-	0.1
6	Myrcene	987	975	1153	0.2 ± 0.0	0.1	0.2
7	*α*-Terpinene	1013	1005	1144	0.3 ± 0.2	0.1	0.5
8	*para*-Cymene	1013	1007	1250	0.4 ± 0.1	0.3	0.6
9	1,8-Cineol	1024	1016	1176	2.0 ± 0.9	0.4	3.2
10	Limonene	1025	1016	1186	0.1 ± 0.1	0.1	0.3
11	*(E)*-*β*-Ocimene	1029	1031	1195	0.1 ± 0.0	0.1	0.1
12	γ-Terpinene	1051	1044	1207	0.5 ± 0.3	0.1	0.9
13	*(E)*-hydrate Sabinene	1053	1048	1232	0.1 ± 0.1	-	0.2
14	Linalol oxyde THF E	1058	1052	1422	0.1 ± 0.1	0.1	0.3
15	Terpinolene	1082	1074	1262	0.2 ± 0.1	0.1	0.3
16	Linalool	1086	1083	1504	15.2 ± 2.1	12.5	19.3
17	*(Z)*-*para*-menth-2-en-1-ol	1108	1104	1542	0.2 ± 0.1	0.1	0.3
18	Camphor	1123	1118	1463	1.3 ± 1.9	0.1	5.3
19	Terpinen-4-ol	1164	1159	1553	1.8 ± 0.6	0.9	2.8
20	*α*-Terpineol	1176	1171	1647	2.7 ± 0.4	2.1	3.4
21	Nerol	1210	1208	1747	0.7 ± 0.3	0.4	1.2
22	Pulegone	1215	1210	1676	0.5 ± 0.3	-	0.7
23	Carvotanacetone	1220	1218	1660	0.5 ± 0.3	-	0.9
24	Geraniol	1235	1234	1794	2.3 ± 0.9	1.4	3.9
25	*(E)*-Anethole	1262	1260	1828	0.2 ± 0.1	-	0.3
26	Carvacrol	1278	1279	2135	0.7 ± 0.4	0.3	1.4
27	*α*-Terpinyl acetate	1335	1330	1686	0.2 ± 0.1	0.1	0.5
28	*(E)*-*β*-Damascenone		1360	1755	0.1 ± 0.1	-	0.3
29	*(E)*-Caryophyllene	1421	1414	1570	0.1 ± 0.0	-	0.1
30	Geranyl acetone	1430	1428	1820	0.1 ± 0.0	-	0.2
31	*δ*-Cadinene	1520	1513	1704	0.1 ± 0.0	0.1	0.1
32	Elemol	1541	1533	2019	0.5 ± 0.1	0.3	0.6
33	*(E)*-Nerolidol	1553	1552	1990	23.0 ± 8.1	8.6	31.5
34	Agarospirol	1635	1614	2143	1.5 ± 0.2	1.1	1.9
35	γ-Eudesmol	1618	1617	2101	1.1 ± 0.3	0.7	1.6
36	β-Eudesmol	1653	1642	2199	34.9 ± 5.3	30	45.6
37	*α*-Eudesmol	1653	1646	2188	0.7 ± 0.4	0.2	1.1
38	2-Pentadecanone	1688	1679	1974	0.5 ± 0.2	0.2	0.7
39	2-Heptadecanone	1884	1881	2179	0.5 ±0.1	0.4	0.7
Total					93.2 ± 1.9	90.8	95.7
	Monoterpene hydrocarbons				2.5		
	Sesquiterpene hydrocarbons				0.2		
	Oxygenated monoterpenes				28		
	Oxygenated sesquiterpenes				62.8		

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

[b] Ir *l* = retention indices on the apolar column (Rtx-1) of littérature;

[c] Ir *a* = retention indices on the apolar column (Rtx-1) ;

[d] Ir *p* = retention indices on the polar column (Rtx-Wax);

[e] Concentration of components (g/100 g) are calculated using Response Factors RFs according to their chemical group (see Table 1) and based on GC peak areas on the apolar column (Rtx-1) except for components with identical RIa (concentration are given on the polar column) ; - = not detected ; min, max = minimum, maximum

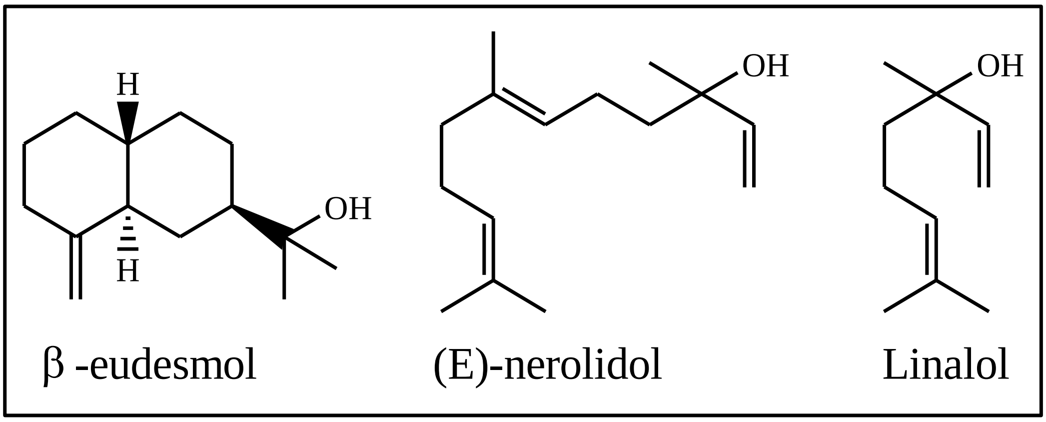

Figure 2. Chemical molecular structure of three major constituents of *W. saharea* essential oils

3.2 Corrosion tests

3.2.1. Effect of Inhibitor Concentration

The effect of addition of by *W. sahrea* essential oil (WS oil) tested at different concentrations on the corrosion of mild steel in 0.5M H_2SO_4 solution was studied by weight loss measurements at 298 K after 6 h of immersion period. The corrosion rate (W) and inhibition efficiency Ew (%) were calculated according to the Eqs. (1) and (2) respectively:

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

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

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).

The values of percentage inhibition efficiency Ew (%) and corrosion rate (W) obtained from weight loss method at different concentrations of WS oil at 298 K are summarized in Table 3.

Table 3. Gravimetric results of mild steel in acid without and with addition of the WS oil at various contents (*t*= 6h, *T*= 298 K).

Inhibitor	Concentration	W (mg/h.cm^2)	E_w (%)
H_2SO_4	0.5 M	1.79	--
	0,25	0,730	59,23
	0,5	0,701	60,87
WS oil	1	0,624	65,13
	1,5	0,550	69,25
	2	0,497	72,19
	3	0,465	74,00

It is very clear that the WS oil inhibits the corrosion of mild steel in 0.5M H_2SO_4 solution, at all concentrations used in this study, and the corrosion rate (W) decreases continuously with increasing additive concentration at 298 K. Indeed, Fig. 3 shown that the corrosion rate values of mild steel decrease when the inhibitor concentration increases while Ew (%) values of WS oil increase with the increase of the concentration reaching a maximum value of 74% at a concentration of 3 g /L. This behaviour can be attributed to the increase of the surface covered θ (E_w %/100), and that due to the adsorption of phytochemical components of the essential oil are adsorbed onto the mild steel surface resulting in the blocking of the reaction sites, and protection of the mild steel surface from the attack of the corrosion active ions in the acid medium. Consequently, we can conclude that the WS oil is a good corrosion inhibitor for mild steel in 0.5M H_2SO_4 solution.

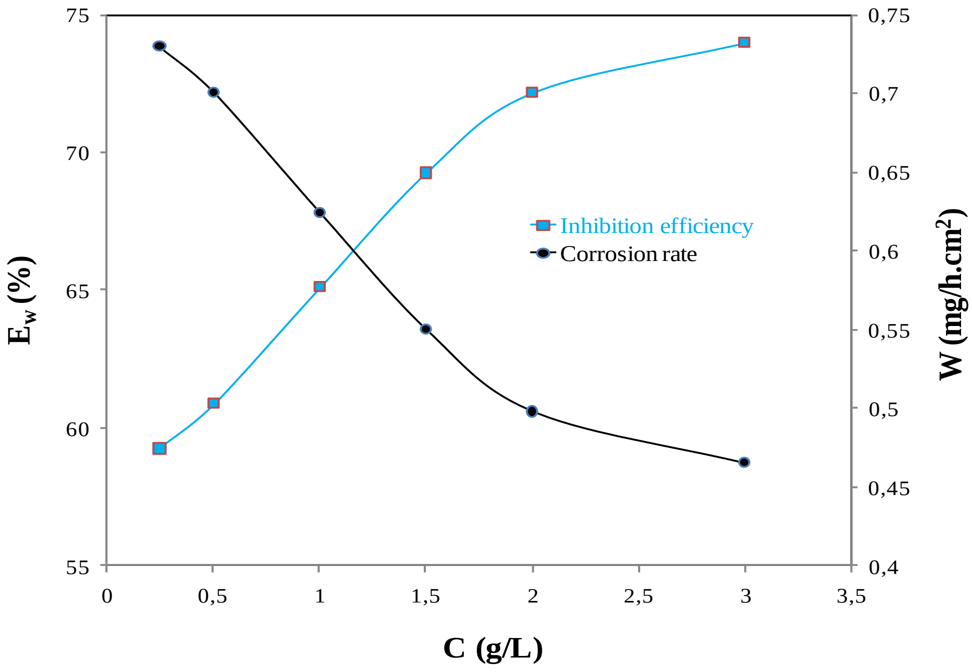

Figure 3. Variation of corrosion rate (W) and inhibition efficiency (Ew) of corrosion of mild steel in 0.5 M H_2SO_4 in the presence of WS oil.

3.2.2. Effect of immersion time

The effect of immersion time on inhibition efficiency is shown in Fig. 4. This figure shows that inhibition efficiency of the WS oil was increased with increasing immersion time, reaching a maximum after 6 h (74%), and then starts to decrease (73.84% at 8 h). The increase in inhibition efficiency up to 6 h reflects the strong adsorption of constituents present in the essential oil on the mild steel surface, resulting in a more protective layer formed at mild steel/sulfuric acid solution interface. Furthermore, with time it seems the inhibiting effect decreases probably because some defects exist on the film leading to the access of aggressive anions to the steel/inhibitor interface. The formation of these weaker sites can be explained with basis in literature [32], where the decrease of the inhibition effciency was attributed to the formation of hemimicelles aggregates by the initially deposited inhibitor molecules, reducing the effective area covered by the inhibitor.

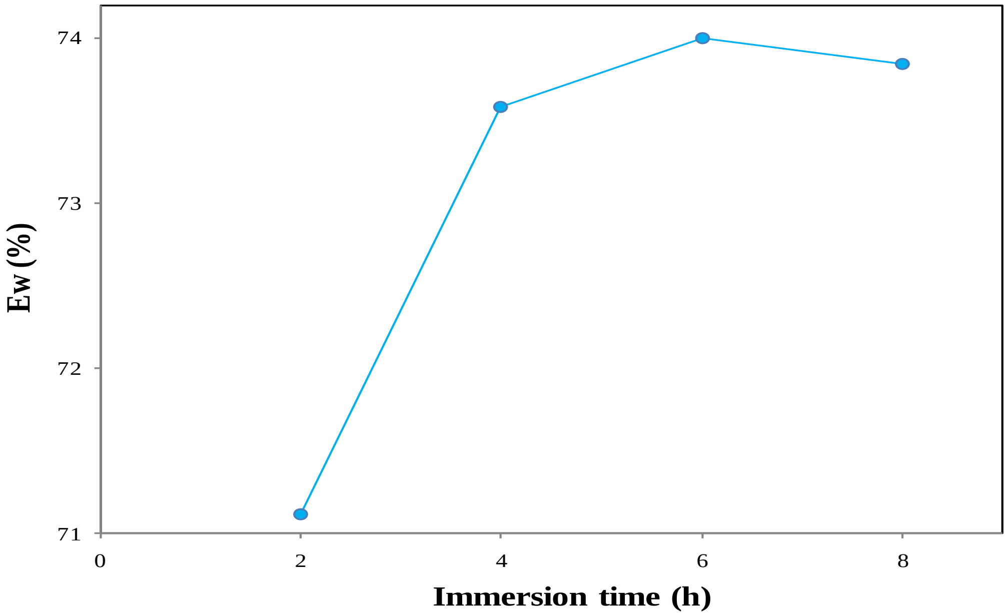

Figure 4. Variation of inhibition efficiency (Ew) of corrosion of mild steel with immersion time in 0.5 M H_2SO_4 in the presence of 3g/L of WS oil.

3.2.4. 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 [33]. The change of the corrosion rate at 3 g/L of the WS oil during 2 h of immersion at different temperatures (303–343 K) was studied in 0.5 M H_2SO_4, both in the absence and presence of WS oil. The data of corrosion rates and corresponding efficiency (Ew) collected were presented in Table 4.

Table 4. Corrosion parameters obtained from weight loss for mild steel in 0.5 M H_2SO_4 containing 3 g/L of WS oil at different temperatures.

T (K)	W ($mg/h.cm^2$)	W_0 ($mg/h.cm^2$)	Ew (%)
303	0,510	1,764	71,06
313	1,123	4,211	73,32
323	1,865	7,125	73,82
333	3,633	14,00	74,05
343	5,477	21,78	74,85

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

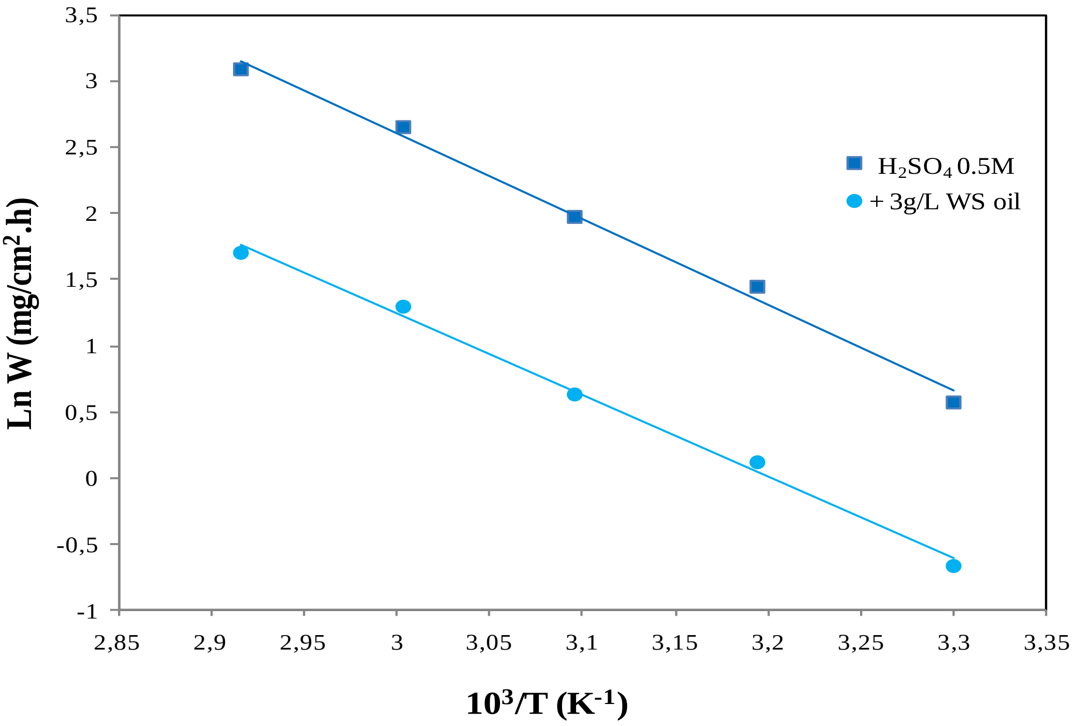

Figure 5. Arrhenius plots for mild steel corrosion rates (W) in 0.5 M H_2SO_4 in absence and in presence of 3 g/L of WS oil.

To calculate activation thermodynamic parameters of the corrosion process, Arrhenius Eq. (3) and transition state Eq. (4) were used [34]:

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

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

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

The apparent activation energy (Ea) was determined from the slopes of Ln (W) *vs* 1/T graph depicted in Fig. 5.

Values of apparent activation energy of corrosion (Ea) for mild steel in 0.5 M H_2SO_4 with the absence and presence of 3 g/L of WS oil were determined from the slope of Ln (W) versus 1/T plots and shown in Table 5.

Fig. 6 shows a plot of Ln (W/T) against 1/T. A 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, are listed in Table 5.

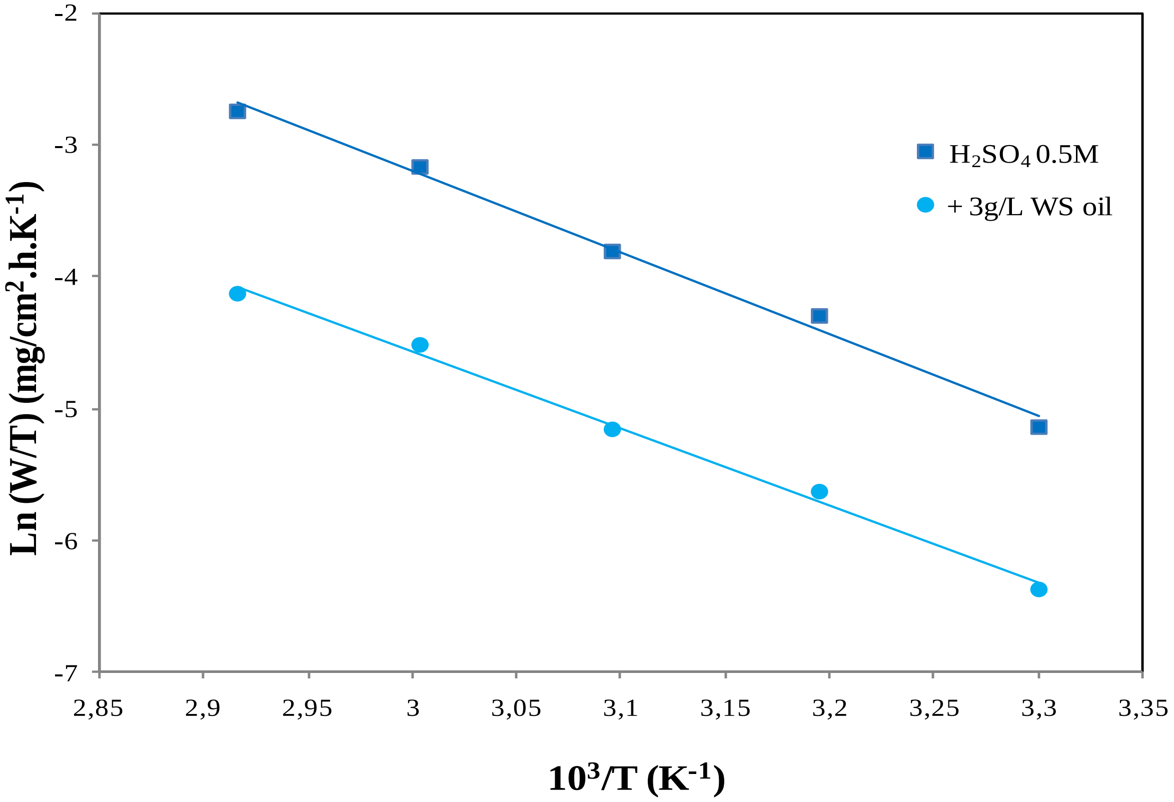

Figure 6. Transition-state plots for mild steel corrosion rates (W) in 0.5 M H_2SO_4 in absence and in presence of 3 g/L of WS oil.

Table 5. Corrosion kinetic parameters for mild steel in 0.5 M H_2SO_4 in the absence and presence of 3 g/L of WS oil.

Inhibitor	**E_a (KJ. mol^{-1})**	**$\Delta H°_a$ (KJ. mol^{-1})**	**$E_a - \Delta H°_a$ (KJ. mol^{-1})**	**$\Delta S°_a$ (J. $mol^{-1}.K^{-1}$)**
H_2SO_4 0.5M	54	51,31	2.69	-70.39
+3 g/L WS oil	51,31	48,62	2,69	-89,77

The calculated values of activation energies from the slopes are 54 and 51.31kJ/mol for free acid and with the addition of 3 g/L of WS oil, respectively. We remark that the activation energy decreases in the presence of inhibitor. This results show that the addition of WS oil decreases metal dissolution in 0.5 M H_2SO_4 medium. Furthermore, the increase of Ew% is explained by Ammar and El Khorafi as chemisorption of inhibitor molecules on the mild steel surface [35]. The lower value of E_a of the corrosion process in an inhibitor's presence when compared to that in its absence is attributed to its chemisorption [36].

Moreover, inspection of the data of Table 5 reveals that the $\Delta H°_a$ values for dissolution reaction of mild steel in 0.5 M H_2SO_4 in the presence of 3 g/L of WS oil are lower (48.62 kJ mol^{-1}) than that of in the absence of inhibitor (51.31 kJ mol^{-1}). The positive signs of $\Delta H°_a$ reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow in the presence of inhibitor [37].

The average difference value of the Ea – ΔHa 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 [38]:

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

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 [39].

3.2.5. Adsorption isotherm

In order to acquire a better understanding of the adsorption mode of the inhibitor on the surface of the mild steel, the data obtained from the three different techniques were tested with several adsorption isotherms, including Langmuir, Frumkin, and Temkin. The Langmuir isotherm(C/θ *vs* C) assumes that there is no interaction between adsorbed molecules on the surface. The Frumkin adsorption isotherm (θ *vs* C) assumes that there is some interaction between the adsorbates, and the Temkin adsorption isotherm (θ *vs* lgC) represents the effect of multiple layer coverage [40].

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

Fig. 7 shows that the relationship between C_{inh}/θ and C_{inh}, at 298 K, yields a straight line with correlation coefficient (R^2) was almost equal to unity (0.998) and all the slopes was very close to unity (1.307). This behaviour suggests that the adsorption of WS oil on mild metal surface followed the Langmuir adsorption isotherm. This isotherm may be written in the following form:

$$\frac{C_{inh}}{\theta} = \frac{1}{b} + C_{inh} \qquad (6)$$

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

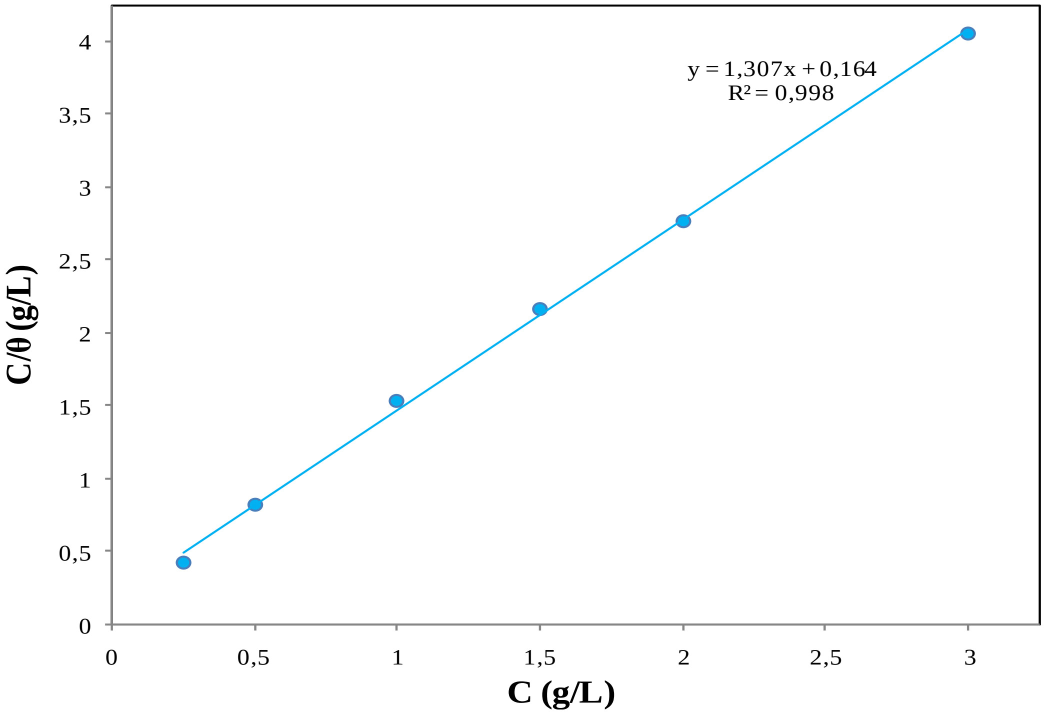

Figure 7. Langmuir adsorption isotherm of WS oil on the mild steel surface.

From the intercepts of the straight lines on the C/θ-axis, b value can be calculated, which are related to the standard free energy of adsorption, ΔG^0_{ads}, as given by the following Eq. (7):

$$b = \frac{1}{55,5}.\exp(-\frac{\Delta G^{\circ}_{ads}}{R.T}) \qquad (7)$$

The standard free energy of adsorption ΔG^0_{ads}, which can characterize the interaction of adsorption molecules and metal surface, was calculated. Generally, values of ΔG^0_{ads} up to -20 kJ mol^{-1}, the types of adsorption was regarded as physisorption, the inhibition acted due to the electrostatic interactions between the charged molecules and the charged metal, while the values around -40 kJ mol^{-}

^{1} or smaller were associated with chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [35].

The value of ΔG^0_{ads} at 298 K, in our measurements, was -14.44 kJ mol^{-1}. The negative value of ΔG^0_{ads} ensures the spontaneity of adsorption process and stability of the adsorbed layer on the surface of the mild steel [41]. The negative value of ΔG^0_{ads} also suggests the strong interactions of inhibitor molecules on mild steel surface and the mechanism of adsorption of WS oil on steel in 0.5M H_2SO_4 was typical physisorption [42]. However, the increase of Ew% with increasing of temperature [303-343 K] is explained by Ammar and El Khorafi as chemisorption of inhibitor molecules on the mild steel surface [35]. Indeed, Ivanov states that increase in Ew% with temperature increase is due to the change in the nature of adsorption: the inhibitor is adsorbed physically at lower temperature, while chemisorption is favored as temperature increases [43].

3.2.6. Mechanism of inhibition of WS oil

The inhibition efficiency increases with essential oil concentrations. This result suggests that the probable mechanism can be explained on the basis of adsorption process and the structure of the constituents present in the essential oil. The inhibition may be due to the adsorption of phytochemical constituents present in the oil by one and/or more of the following two modes: In one mode, the neutral molecules may be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the oxygen atoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis of donor–acceptor interactions between π-electrons of the aromatic ring and vacant d-orbitals of surface iron atoms. In second mode, since it is well known that the mild steel surface bears positive charge in acid solution [44], it is difficult for the protonated molecules to approach the positively charged mild steel surface (H_3O^+/metal interface) due to the electrostatic repulsion. Since SO_4^{2-} have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, the protonated inhibitors adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus, there is a synergism between adsorbed SO_4^{2-} ions and protonated inhibitors. Thus, inhibition of mild steel corrosion in 0.5 M H_2SO_4 is due to the adsorption of phytochemical constituents on the mild steel surface [45,46].

Presumably, the adsorption of *W. sahare* essential oil is only made by β-Eudesmol, Nerolidol-E and Linalool which are the most abundant compounds. However, a synergistic or antagonistic effect of other molecules may play an important role on the inhibition efficiency of this oil.

4. CONCLUSION

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

(1) Chemical analysis shows β-Eudesmol **36** (34.8%), Nerolidol-E **33** (23.6%) and Linalool **16** (15.4%) can be the major components of *W. sahrea* essential oil. These three compounds represent 73.1% of the total oil.

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

(3) *Warionia saharea* essential oil acts as good inhibitor for the corrosion of mild steel in 0.5M H_2SO_4 with an inhibition efficiency 74% at 3g/L;

(5) Inhibition efficiency on mild steel may occur by action of three abundant compounds.

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