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Chemical composition, antioxidant and anticorrosion activities of Mentha Suaveolens

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Abstract

The chemical composition of essential oil of M. suaveolens isolated from Al Hoceima National Park, Morocco was performed by CG/SM, and a total of 43 components were identified. The essential oil was characterized by Piperitenone oxide (44.3%) as a mainly constituent. The other major components were Z-Piperitone oxide (19.1%), Terpinen-4-ol (3.8%), 1,2-Epoxymenthyl acetate (3,5%) and trans-hydrate Sabinene (3.1%). The aqueous extract was screened for his activity antioxidant by DPPH free radical scavenging. It has showed a moderate reducing power against acid ascorbic and BHA as standards. The essential oil (MSO) and the aqueous extract (MSE) are also screened for their inhibition aptitude as potential green corrosion inhibitors of mild steel for acidic media. the effect of inhibition has been studied using weight loss measurements and electrochemical techniques (potentiodynamic polarization curves, and electrochemical impedance spectroscopy) in the presence of different concentrations of MSO & MSE ranging from 0.25 g/L to 2 g/L. Potentiodynamic polarization showed that MSE and MSO behaves as mixed type inhibitors. Adsorption of M. Suaveolens on the steel surface followed a Langmuir's isotherm and the thermodynamic parameters were determined and discussed.

1. Introduction

The species studied is native to Southern and Western Europe, extending northwards to The Netherlands, cultivated as a pot-herb and naturalized in Northern and Central parts of Europe. It is generally found along streams, bogs and humid places [1]. M. suaveolens has been used in the traditional medicine of Mediterranean areas and has a wide range of effects: hypotensive, stimulating, stomachic, carminative, choleretic, antispasmodic, sedative, tonic, anti-convulsive, insecticidal, etc. It is also useful in cases of cough, nausea, anorexia and bronchitis [2] and finds application in digestion problems, influenza, respiratory ailments, rheumatism, skin diseases and irritation [3]. It shows depressor, analgesic, anti-inflammatory, cytotoxic, hepatoprotective and antifungal activities [4-6].

Currently, plant extracts are viewed as an incredibly rich source of natural chemical compounds, which can be extracted by simple and low-cost procedures and which are biodegradable in nature. The abundant phytochemical constituents of plant extracts possess considerable potential as a natural antioxidants and anti-corrosives inexpensive and non-toxic. Nowadays, researchers focus their attention in order to develop environmentally friendly corrosion inhibitors exhibiting a strong affinity for metal surfaces and low environmental risk [7-14].

Owing to the aggressiveness of acidic mediums, a significant economic loss is suffered by the concerned industries resulting from rapid corrosion of metallic parts. Iron and alloys are the most consumed materials and extensively used for constructional, industrial and numerous engineering applications [15]. However, these materials in inquiry are susceptible to corrosion, especially in acid media. The isolation of a metal from corrosive agents using organic inhibitors in acidic media is one of the challenging topics of current research in various industries involving chemical cleaning, descaling, pickling, acid oil-well acidizing, etc., [16-22].

However, as a result of their high cost and increasing awareness of health and ecological risks, consideration is being drawn towards finding highly efficient, cheaper and non-toxic inhibitors.
The yield of these natural products as well as the corrosion inhibition abilities of the plant extracts vary widely depending on the part of the plant and its location [23]. Extract of different parts of plant like root, seeds, leaves, stem, flower and fruits can be used as inhibitor to reduce the corrosion rate of various ferrous and non-ferrous metals in acidic media.
The aim of this study is to evaluate the inhibition effect of M. suaveolens oil (MSO)and its extract (MSE) on corrosion behavior of mild steel in 0.5 M H_2SO_4 using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The adsorption and inhibition efficiency of these inhibitors were investigated and the thermodynamic parameters in both the absence and the presence of these inhibitors were calculated.

2. Experimental Details

2.1. Materials

Corrosion specimens carried out using a mild steel of the composition of 0.09 % P, 0.38 % Si, 0.01 % Al, 0.05 % Mn, 0.21 % C, 0.05 % S, and balance Fe. The rectangular specimens 1 cm × 1.5 cm × 0.02 cm in size were mechanically polished with emery paper up to 1200 grade, then cleaned in ultrasonic bath with ethanol, rinsed with bidistilled water and finally dried at room temperature (298 ± 1K). The electrolyte solution, H_2SO_4 was prepared by diluting a Merck analytical commercial grade 98 % H_2SO_4 with deionized water.
Fresh aerial parts of M. suaveolens were collected during Jun from the area of Al Hoceima National Park, Morocco (35° 20′ 00″ Nord, 4° 00′ 00″ Ouest). They were washed with tap water and deprived of dusts prior to extraction. The essential oil tested was extracted with the Clevenger type apparatus from the dried aerial parts according to the method recommended in the European Pharmacopoeia[24]. Stock plant extract was prepared by an aqueous maceration and was performed on 0.2 g of plant with 100 mL of 0.5M H_2SO_4 solution for 24 h. After filtration, the extract was recovered.

2.2. Determination of total phenolic content of extract

Determination of polyphenolic content was performed with the Folin-Ciocalteu colorimetric reagent [25]. This method based on the reduction in an alkaline medium of the mixture phosphotungstic (WO_4^{2-}) / phosphomolybdic (MoO_4^{2-}) by the oxydable phenolics compounds. Briefly1 ml of a reagent Folin Ciocalteau (10%) was added to 0.2 ml of aqueous extract. After 4 min of incubation, 0.8 mL of Na_2CO_3 (75 g/L) was added to mixture. After 30 min of standing at room temperature in dark, the absorbance was measured at 765 nm.
Phenolics contents are expressed as gallic acid equivalent per gram of powder (the equation regression was $y = 0,0052.x + 0,0258,\ r^2 = 0,9957$).

2.3. Estimation of total flavonoids content of extract

To quantify the flavonoids contained in the extract of the plant studied, aluminum chloride colorimetric method was used [26]. This method is based on the formation of acid labile complexes between ortho - hydroxy groups in A or B-ring of flavonoids and aluminum chloride. The solution of test was contained 1 ml of each sample and standard (quercetin) and1 mL of $AlCl_3$ (2% in ethanol). The mixture was remained at room temperature for10 min in dark. Then, the absorbance was measured at 430nm. This assay was realized in triplicate.
In this method, quercetin was employed to build the calibration curve ($y = 0,0344.x + 0,0088,\ r^2 = 0,991$). Then, the flavonoids content were expressed as quercetin equivalent per gram of powder.

2.4. *Determination of total flavonols content of extract*

The assay is performed in a test tube. 2.8 ml of distilled water, 0.1 ml of $AlCl_3$, 0.1 ml of CH_3CO_2K (1 M), 0.5 ml of the extract are mixed, then incubated in the shade at room temperature for 30 minutes [27]. Absorbance was read at 415 nm. All determinations were carried out in triplicate. The flavonol content is expressed in milligrams quercetin equivalent per gram of powder (the equation regression was $y = 0,008.x - 0,016,\ r^2 = 0,998$).

2.5. DPPH radical scavenging activity

The ability of the bioactive compounds of plant extract to scavenge the stable 1,1-diphenyl-2 -picryl hydrazyl radical (DPPH) was assessed by the standard method a slightly modified DPPH free radical scavenging assay [38]. The ethanolic solution of the aqueous extract was prepared with a concentration of 1 m / mL. Thus, appropriate dilutions were prepared ranging from to 5 to 100 µg/mL.

In a test tube, 1.9 mL of DPPH solution was added to 0.1 ml of aqueous extract. The samples were first kept in a dark place at room temperature and their absorbance was read at 517 nm after 30 min. The scavenging activity DPPH radical was expressed as percentage inhibition by the following formula:

$$\left[\left(A_{blank} - A_{sample}\right) / A_{blank}\right] \times 100 \quad (1)$$

Where, A_{sample} is the absorbance of the solution containing the sample at 515 nm, and A_{blank} is the absorbance of the DPPH solution. The IC_{50} values were calculated as the concentration of extract causing a 50% inhibition of DPPH radical.

2.6. Weight loss measurements

In brief, mild steel specimens were immersed for 6hinthe absence and presence of different concentrations of M. suaveolens at different range of temperature. The specimens were carefully washed in double-distilled water, dried and then weighed. Duplicate experiments were performed in each case to assure the consistency of the results and the average values of weight losses were taken for calculation. The following equations were used to determine the inhibition efficiency (IE%) and surface coverage (θ):

$$IE\ \% = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \quad (2)$$

$$\theta = \frac{IE\%}{100} \quad (3)$$

where W_{corr} and W'_{corr} are the corrosion rate of steel in 0.5M H_2SO_4 in the absence and the presence of inhibitor, respectively.

2.7. Electrochemical measurements

Electrochemical measurements were carried out using a potentiostat PGZ100 piloted by Voltamaster soft-ware. The corrosion cell used had three electrodes. A saturated calomel electrode (SCE) was used as reference, platinum electrode as auxiliary electrode with surface area of 1 cm2 and the working electrode (WE) was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to establish a steady state open circuit potential (E_{corr}). The test solution was thermostatically controlled at 308 K in air atmosphere without bubbling. All potentials were measured against SCE.

Potentiodynamic polarization curves were plotted at a polarization scan rate of 1 mV/s. The polarization curves are obtained in the potential range from −800 mV to −200 mV at 308 K. The EIS experiments were conducted in the frequency range of 100 kHz to 10 mHz, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. Before recording the curves the test solution is de-aerated in magnetically stirred for 30 min in the cell with nitrogen.

3. Results and discussion

3.1. M. suaveolensoil analysis

The analysis of M. suaveolens essential oil was performed by CG/SM, it has allowed the identification of 43 components, which accounted for 96.8% in the total of oil. Their retention indices (RIs) and their relative percentages are reported in Table 1.The essential oil was characterized by high amounts of Piperitenone oxide (44.3%). The other major components were Z-Piperitone oxide (19.1%), Terpinen-4-ol (3.8%), 1,2-Epoxymenthyl acetate (3,5%) and trans-hydrate Sabinene (3.1%). The 38 other compounds are reported in low amounts.

Presently, it is well known that the chemical composition of the same taxon growing in different zones can have very different chemotypes and hence different biological properties. However, there is a great interest to screen the plants used therapeutically in different regions of the world [39].Another investigation on Moroccan plant material from Azrou, Tetouan and Meknès confirmed the prevalence of Piperitenone oxyde (74.69%, 41.84% and 34%, respectively), while that from M'rirt is rich both in Piperitenone oxyde (81.67%) and piperitenone (10.14%) [40,41].

Identification of essential oil ingredients was the subject to numerous studies which have shown a difference in its constituents depending on the region of origin [42-46]. In the fact this difference can be attributed to several factors as the period of harvested, the period of sunshine, the nature and the composition of the ground [37].

Table 1. Chemical constituents of M. suaveolens oil (%)

Composés	IL	Ir /apol	Ir /pol	%
α-Pinene	936	931	1026	0.6
Camphene	950	943	1062	0.4
1-Octen-3-ol	962	962	1447	0.7
Sabinene	973	966	1123	0.4
β-Pinene	978	971	1107	0.7
Myrcene	987	982	1155	0.5
p-Cymene	1015	1014	1271	0.4
Limonene	1025	1023	1199	1.4
Z-b-Ocimene	1029	1027	1233	0.1
γ-Terpinene	1051	1050	1211	0.3
trans-hydrate Sabinene	1053	1055	1461	3.1
Non-1-en-3-ol	1058	1064	1446	0.1
cis-hydrate Sabinene	1082	1084	1543	0.3
1-Octen-3-yl-acetate		1095	1378	0.6
cis-p-Menth-2-en-1-ol	1108	1109	1576	0.2
cis-p-Mentha-2.8-dien-1-ol	1113	1118	1644	0.2
Borneol	1150	1152	1698	2.4
p-Cymen-8-ol	1169	1165	1842	0.4
Terpinen-4-ol	1164	1166	1600	3.8
α-Terpineol	1176	1175	1692	0.4
E-Piperitone oxyde	1232	1233	1703	1.2
Z-Piperitone oxyde	1232	1233	1725	19.1
Bornyl acetate	1270	1272	1579	0.2
Thymol	1267	1274	2177	1.0
Piperitenone	1318	1313	1911	0.4
Piperitenone oxyde	1335	1339	1949	44.3
Z-Jasmone	1371	1371	1935	0.3
α-Copaene	1379	1380	1495	0.1
Nepetalactone	1360	1380	1992	1.2
β-Elemenene	1389	1390	1592	0.2
1.2-Epoxymenthyl acetate		1390	1883	3.5
trans-Caryophyllene	1421	1421	1565	2.1
E-β-Farnesene	1446	1450	1670	0.4
α-Humulene	1455	1452	1670	0.3
cis-Muurola-4(15).5-diene	1462	1460	1672	0.5
Germacrene D	1479	1479	1709	2.4
γ-Cadinene	1507	1508	1758	0.2
Calamenene	1517	1512	1829	0.3
δ-Cadinene	1520	1517	1758	0.2
Caryophyllene oxyde	1578	1572	1976	0.4
Viridiflorol	1592	1583	2077	0.7
1.10-diepi Cubenol	1615	1604	2052	0.3
α-Cadinol	1643	1641	2225	0.5
			TOTAL	96.8

3.1. Determination of total phenolic content (TPC), total Flavonoids (TF) and Flavonols

Phenols bioactive compounds such as Flavonoids and Flavonols are the major secondary metabolites present in the plant kingdom. They have been reported to be as reducing agents, hydrogen donators, and singlet oxygen

quenchers. They have also metal chelation properties. Those properties will allow it to be excellent antioxidants [28-30]. Thus, the TPC, TF and flavonols of the plant extract studied were evaluated by different methodsand listed in Table 2.

Table 2 Phenolic compounds of aqueous extract of M. suaveolens

Compound	TPC [a]	TF [b]	FV [c]
MSE[d]	145.86 ± 7.48	30.57 ± 2.13	16.50 ± 1.13

All the values are mean ± SD; SD: standard deviation
[a]TPC: total phenolic compounds (mg GAE/g powder)
[b]TF: total flavonoids (mg QE/g powder)
[c]FV: Flavonols (mg QE/g powder)
[d]MSE: Menthe Sauvelones Extract

0.2. Scavenging activity of DPPH radical

Several studies have been proved that the antioxidant activity of compounds derivatives from plant kingdom is correlated to polyphenols compounds. These compounds are efficient and have ability to protect organisms from damage caused by free radical -induced oxidative stress. In the present work DPPH free radical was investigated to valorizefree radical scavenging activity (RSA). The results of extract aqueous and positive control (acid ascorbic) are presented in Table 3. Fig. 1 shows that radical scavenging activity (RSA, %) increased with increasing amount of the extract and positive controls (acid ascorbic and BHA). From the IC_{50} value of aqueous extract (23.49µg/mL) we conclude that his scavenging activity is lower than that exhibited from acid ascorbic (2.82µg/mL) and that of BHA (6.80 µg/mL).

Table 3DPPH radiacl scavenging activity of aqueous extract of M. suaveolens

Samples	Scavenging ability (%, Mean ± SD), concentration (µg/mL)						
	5.0	10.0	20.0	30.0	40.0	50.0	100.0
MSE[a]	14,9 ± 1,2	25,8 ± 1,0	44,1 ± 1,3	62,1 ± 1,1	79,9 ± 1,4	89,2 ±0,7	89,7 ± 1,2
BHA[b]	51,0 ± 1,6	65,9± 1,5	83,1± 0,9	87,5± 0,1	88,5 ± 1,0	89,0± 1,2	89,8 ± 0,7
Asc. Ac[c]	85,3 ± 1,3	93,0± 1,7	93,2± 1,2	93,4± 1,1	93,4± 1,5	93,8± 1,0	94,3± 1,0

[a]See the note in Table 2 for the full name of extract
[b]BHA: Butylated hydroxytanisole;
[c] Asc. Ac: Ascorbicacid

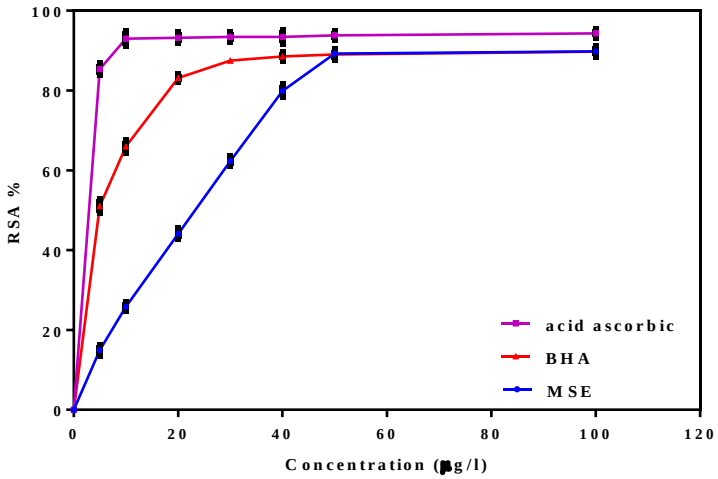

Figure 1. Radical Scavenging Activity of MSE

0.3. Weight loss measurements

0.3.1. Effect of inhibitor concentration

Gravimetric measurements of steel were investigated in 0.5M H_2SO_4in the absence and the presence of various concentrations of MSE and MSO at 6 h of immersion and 308 K.Table 4 summarizes the corrosion parameters such as surface coverage (θ), inhibition efficiency (IE%) and corrosion rate (W_{corr}).

Table 4 Gravimetric results of mild steel in 0.5 M H_2SO_4 at different concentrations of MSE & MSO.

Temp (K)	Con (g/L)	Surface coverage (θ)		Inhibition Efficiency (%)		Blank	W ($mg.cm^{-2}.h^{-1}$)	
		MSO[a]	MSE	MSO	MSE		MSO	MSE
308						0.520		
	0.25	0,611	0,823	61.1	82.3		0.202	0.092
	0.5	0,653	0,850	65.3	85.0		0.181	0.078
	1	0,730	0,870	73.0	87.0		0.141	0.068
	2	0,820	0,951	82.0	95.1		0.094	0.025
313	2	0,673	0,733	67.3	73.3	0.890	0.237	0.290
323	2	0,467	0,588	46.7	58.8	1.350	0.255	0.719
333	2	0,381	0,504	38.1	50.4	2.850	1.115	1.762
343	2	0,173	0,451	17.3	45.1	5.830	3.200	4.718

[a]MSE: Menthe Sauvelones Oil

Results obtained from gravimetric measurements listed in the Table 4, show that the inhibition efficiency (IE%) increases to attain82.0% and 95.1% for MSO and MSE at 2g/L, respectively, and the corrosion rate decreases with the increase of concentration of the tested inhibitors. Finally, we can note that,this fact could be expressed that the inhibitive action of inhibitors is through adsorption on the mild steel surface which is enhances with respect to the inhibitor concentration. The adsorption of active compounds existing in the extracts, on mild steel diminishes the surface area offered for corrosion.

0.3.2. Effect of temperature

In order to give more insightintothe adsorption behavior of M. suaveolens inhibitors, the effect of temperature(Table 4) has been studied by weight loss measurements in the range of 313–343 K temperature during 1 h of immersion. The corresponding results are given in Table 4.

Inspection of data illustrated in Table 4 showed that the increase of corrosion rate is more marked with the rise of temperatureand the inhibition efficiency decreases to attain a value of 17.3% and 45.1% at 343 K for MSO and MSE at 1h immersion period. Alternatively, the slightly decrease on inhibition efficiency with temperature can be justified by the decrease of the strength of adsorption processes at high temperature [31].

0.3.3. Kinetic-thermodynamic parameters

The thermodynamic parameters obtained from the kinetic model such as the apparent activation energy E_a , the enthalpy of activation ΔH_a^o and the entropy of activation ΔS_a^o for corrosion of mild steel in the absence and presence of different concentrations of M. suaveolens were calculated from Arrhenius Eq. (3) and transition state Eq. (4) in the temperature range from 313 to 343 K [32]:

$$LnW = LnA - \frac{E_a}{R.T} \tag{4}$$

where E_a represents the apparent activation energy, R gas constant, T the absolute temperature, A the pre-exponential factor and W the corrosion rate, obtained from the weight loss method.

$$LnW = \left[Ln\left(\frac{RT}{Nh}\right) + \left(\frac{\Delta S_a^o}{R}\right)\right] - \frac{\Delta H_a^o}{RT} \tag{5}$$

where W refers to the corrosion rate, R the gas constant, T the absolute temperature, A the pre-exponential factor, h is Plank's constant and N is Avogadro's number.

Arrhenius plots of Ln(W) vs 1000/T gave a straight line with slope of ($-E_a/R$) and intercept of (LnA) are shown in Fig. 2. All the linear regression coefficients are close to 1, indicating that corrosion of mild steel in 0.5 M H_2SO_4 can be elucidated using the kinetic model.

The values of E_a were determined in solutions containing M. suaveolens inhibitors and found to be higher than uninhibited solution in the presence of MSO and MSE that designates the good performance of these inhibitors at higher temperatures. Generally, the addition of compounds to the corrosive solution is accompanied by an increase in activation energy value when compared to the blank, which may often be interpreted as an indication for the formation of an adsorptive film by a physical (electrostatic) mechanism [43, 44].

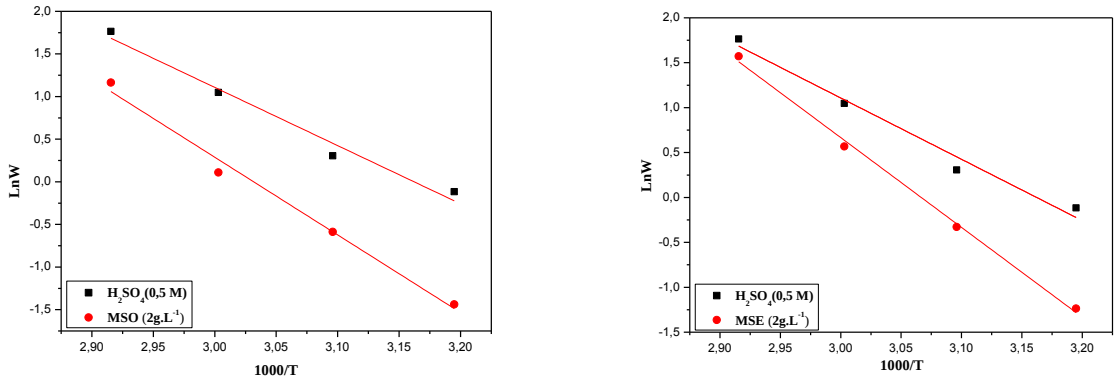

Figure 2: Arrhenius plots of mild steel for 2 g/L of MSE and MSO in 0.5 M H_2SO_4.

Table 5 Activation parameters for steel in 0.5 M H_2SO_4 in the absence and presence of MSE and MSO.

Inhibitors	E_a	ΔH_a $k\ j.mol^{-1}$	ΔS_a $j.K^{-1}.mol^{-1}$	$E_a - \Delta H_a$
Blank	56.7	54.0	-74.4	2.7
MSE	75.7	73.0	-24.3	2.7
MSO	83.0	80.3	00.8	2.7

The relationship between Ln(W/T) and 1000/T is shown in Fig. 3. Straight lines are obtained with a slope of ($-\Delta H_a / R$) and an intercept of ($\left(\mathrm{Ln\,R/Nh} + \Delta S_a / \mathrm{R}\right)$) from which the values of ΔH_a and ΔS_a are calculated and are given in Table 5. Examination of thermodynamic parameters data revealed, that the positive values of ΔH_a reflect the endothermic nature of metal dissolution process. Moreover, it is well remarked that the value of E_a is larger than the analogous value of ΔH_a indicating that the corrosion process involved a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume [45]. Furthermore, for MSE and MSO the average difference value of the $E_a - \Delta H_a$ is 2.7 kJ/mol, which is approximately equal to the average value of RT (2.61 kJ/mol). Therefore, it is indicated that the corrosion process is a unimolecular reaction as it is characterized by the following equation:

$$E_a = \Delta H_a - RT \tag{6}$$

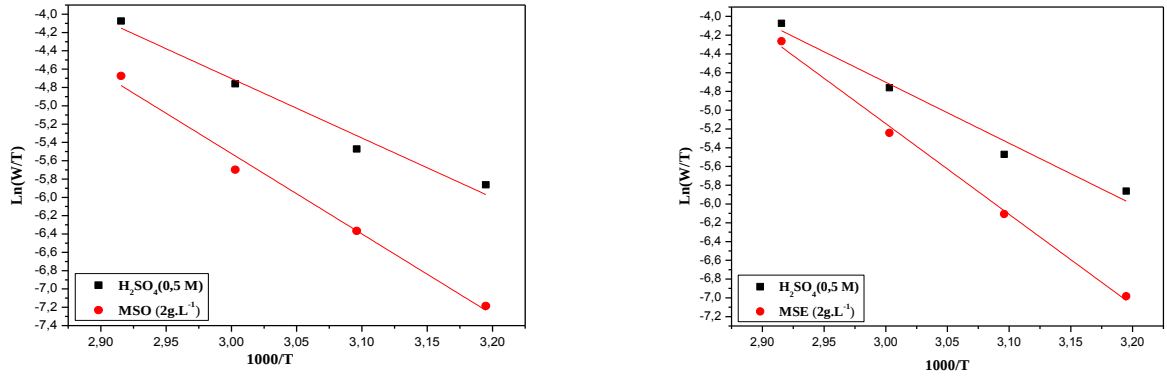

Figure 3: The variation of Ln (W/T) ~ f (1000/T) of the steel in 0.5 M H_2SO_4 with and without MSE and MSO.

The values of ΔS_a^o in the presence of M. suaveolens inhibitors tested were higher than uninhibited solution. And the negative values 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 and suggesting that the dissolution reaction will be more blocked sites from the metal surface [46].

3.3.4. Adsorption isotherm

Adsorption isotherm gives necessary information about the interaction between the inhibitor and metal surface. The θ values of different concentrations of inhibitor were tested by fitting to various isotherms including Frumkin, Langmuir, Temkin, Freundlich, Bockris-Swinkles and Flory Huggins isotherms. Langmuir adsorption isotherm was found to provide best description of the adsorption behavior of the investigated inhibitor. The Langmuir isotherm is given by the equation [47]:

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

With $K = \frac{1}{55.5}.\exp\left(-\frac{\Delta G_{ads}}{R.T}\right)$ (8)

Where C is the inhibitor concentration, θ the fraction of the surface covered determined by IE%/100, k the equilibrium constant, ΔG_{ads} is the standard free energy of adsorption reaction, 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. Fig. 4 show the dependence of the ratio C/θ as function of C for MSE and MSO respectively.

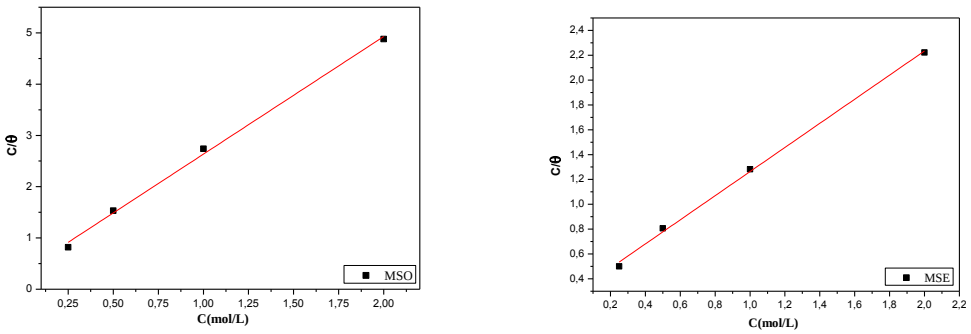

Figure 4: Plots of Langmuir adsorption isotherm of MSO and MSE on the steel surface at 308 K

0.4. Tafel polarization measurements

To elucidate the kinetic of inhibition reactions for inhibitors studied. Polarization study has carried out to get knowledge. Potentiodynamic curves are recorded in the presence and the absence of inhibitors, after pre-polarizing the electrode at its E_{corr} for 30 min, thereafter pre-polarized at -800 mV for 10 min. After this scan, the potential was swept stepwise from the most cathodic potential to the anodic direction.

Tafel plots of steel in 0.5 M H_2SO_4in the presence and the absence of the tested inhibitors are shown in Fig. 5.

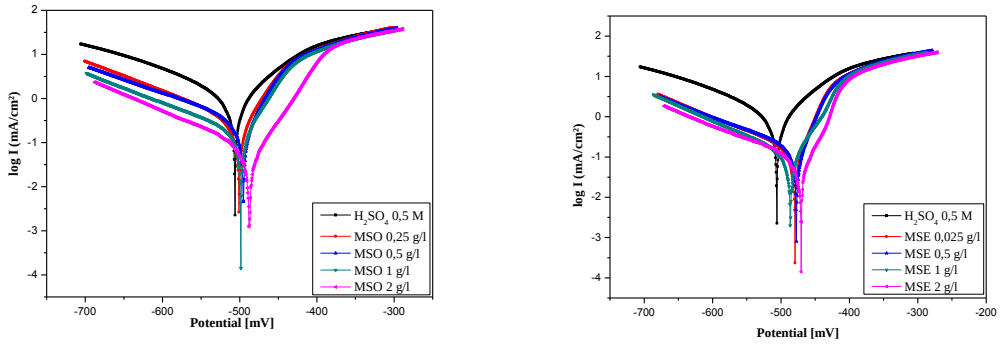

Figure 5: Cathodic and Anodic polarisation curves of mild steel in 0.5 M H_2SO_4in the presence of M. suaveolens oil and its extract at different concentrations.

The respective electrochemical parameters derived from the plots including corrosion current densities (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c) and inhibition efficiency (IE %) are given in Table 6.

Based on data given in Table 6, the inhibition efficiencies (IE%),were calculated using the equation [48]:

$$IE\% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \quad (9)$$

Where I_{corr} and I'_{corr} are, respectively the uninhibited and inhibited current density. The corrosion current density was calculated from the intersection of cathodic and anodic Tafel lines.

Table 6. Electrochemical parameters of steel at various concentrations of MSE and MSO respectively in 0.5 M H_2SO_4 and the corresponding inhibition efficiencies.

Inhibitors	Concentrations (g/l)	I_{corr} ($\mu A/cm^2$)	$-E_{corr}$ (mV)/SCE	$-b_c$ (mV/dc)	θ	IE%
blank	0.5 M	901,7	506	194.0	-	-
MSO	0.25	309,3	500.8	154.4	0,657	65.7
	0.5	296,9	495.3	162.1	0,670	67.0
	1	153,1	498.6	143.8	0,830	83.0
	2	73,9	487.3	133.5	0,918	91.8
MSE	0.25	137,7	477.4	146.9	0,847	84.7
	0.5	128,3	479.6	132.8	0,857	85.7
	1	107,8	496.2	132.1	0,880	88.0
	2	59,7	470.8	134.4	0,933	93.3

Inspection of polarization curves and electrochemical parameter listed in Table 6, reveals that that I_{corr} values were progressively reduced in the presence of inhibitors with steady increase in the concentration from 901.7 to 73.9 and 59.7µA/cm^2 with the highest concentration of MSO and MSE (2 g/L). The obtained efficiencies (IE%) indicate that M. suaveolens inhibitors act as an effective inhibitors. The values of (IE%) increase with the inhibitors concentration to achieve 91.8% and 93.3% for MSO and MSE, respectively at 2 g/L. It is well illustrated from the data listed in Table 6 that, the adding of M. suaveolens inhibitors to the acidic medium inhibits both anodic metal dissolution and cathodic hydrogen evolution reactions. The lower corrosion current density I_{corr} values in the presence of inhibitors without causing significant changes in corrosion potential $(-506.0 \le E_{corr} mV/SCE \le -470.8)$ suggests that, the compound is mixed type. An inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV/SCE, with respect to corrosion potential of the blank. The presence of inhibitors does not prominently shift the corrosion potential compared to the blank (5.2–35.2) mV/SCE, this confirms that the studied inhibitors (MSO & MSE) act as a mixed-type inhibitor [50]. Furthermore, inhibitors may be adsorbed on the surface, thereby blocking the corrosion reaction.

0.5. Electrochemical impedance spectroscopic studies

EIS has been also used for the examination of inhibition performance of M. suaveolens inhibitor of steel in 0.5 M H_2SO_4 solution at 303 K after 30 min of immersion. Nyquist plots of mild steel in uninhibited and inhibited acid solutions containing different concentrations of MSO and MSE are shown in Fig.6.

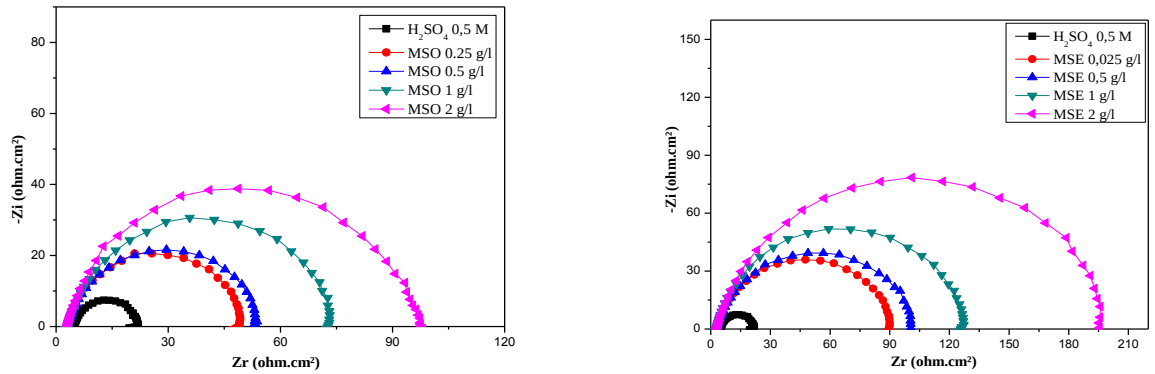

Figure 6: Nyquist diagrams for steel electrode with and without M. suaveolens after 30 min of immersion.

Generally, Fig. 6 shows that the impedance diagrams exhibit one single depressed semicircle indicating a charge transfer process mainly controls the corrosion of mild steel. The diameter of semicircle increases with the inhibitor concentration. This fact is attributed to the inhibition effects of M. suaveolens inhibitors. Based from data given in Table 7, it is also clear that the charge-transfer resistance (R_t) values increase with inhibitor

concentration and as a result the inhibition efficiency increases to 81.9% and 91.3% for MSO and MSE at 2 g/L, respectively. Inspection of the electrochemical and EIS parameters denotes that the values of the numerous parameters such as corrosion potential, anodic and cathodic Tafel slopes vary slightly in the presence of inhibitors studied. These results suggest that the action of molecules of M. suaveolens inhibitors act by pure geometric blocking of the electrode surface.

Table 7 Impedance parameters for corrosion of steel in acidic medium at various contents of MSO and MSE respectively

Inhibitors	Concentrations (g/L)	R_t ($Ohm.cm^2$)	C_{dl} ($\mu F.cm^{-2}$)	f_{max} (Hz)	θ	IE%
Blank	1M	17	187,3	50.00	-	-
M. suaveolens Oil	0.25	46.50	85.6	40.00	0.634	63.4
	0.5	51.00	78.0	40.00	0.666	66.6
	1	70.82	71.0	31.64	0.760	76.0
	2	94.15	53.4	31.64	0.819	81.9
M. suaveolens Extract	0.25	88.25	90,21	20.00	0.807	80.7
	0.5	99.37	80,1	20.00	0.829	82.9
	1	125.4	80,2	15.82	0.868	86.8
	2	196.3	51.2	15.82	0.913	91.3

Conclusion

M. suaveolens was valorized as a green effective inhibitor to inhibit the corrosion of mild steel in 0.5 M H_2SO_4 solution by weight loss measurement, EIS and current–potential measurements. The results obtained lead to the following conclusions:

- The chemical composition of essential oil by GC/MS isolated from M. suaveolens plant shows that it's dominated by Piperitenone oxide, Z-Piperitone oxide, Terpinen-4-ol, 1,2-Epoxymenthyl acetate and trans-hydrate Sabinene (44.3%, 19.1%, 3.8%, 3,5% and 3.1%, respectively).
- The polarization studies showed that SMO and MSE inhibit both cathodic hydrogen reduction reactions and anodic metal dissolution, and then they act as mixed-type inhibitors of corrosion
- The inhibition efficiency of MSE and MSO increases with the increase of inhibition concentration.
- The adsorption of the M. suaveolens compounds on the mild steel surface in 0.5 M H_2SO_4 solution obeys Langmuir adsorption model.
- The values of inhibition efficiencies obtained from the different independent quantitative techniques used show the validity of the results.

M. suaveolens inhibitors being natural and environmentally benign products, they can be used as an alternative for toxic chemical inhibitors in acidization and acid pickling of mild steel.

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