

Composition of *Piper Nigrum L*. Essential Oils Extracted by Classical Hydrodistillation and Microwave-assisted Hydrodistillation and Inhibitory Effect on the Corrosion of mild steel in hydrochloric acid

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Abstract

The inhibition of the corrosion of mild steel in 1 M HCl by the seeds essential oil of *piper nigrum*; extracted through microwave-assisted hydrodistillation (MHD) and conventional hydrodistillation (CHD) method; has been studied using weight loss, potentiodynamic polarization method and electrochemical impedance spectroscopy measurements at different concentrations and effect of temperature. Three amounts of essential oils obtained by classical hydrodistillation and by microwave hydrodistillation on low and high microwave power are tested on the corrosion inhibition of mild steel. The measurements show that inhibition efficiencies increase with the increasing concentration of the inhibitor. The results of weight loss studies correlated well with those of impedance and polarization studies. The maximum inhibition efficiency (95.99%) was found at 0.6g/L at 308 K, after 6 h as immersion time. This reveals that inhibitive action of the inhibitor was mainly due to adsorption on the mild steel surface and blocking of the active sites. The above results showed that inhibitor acted as a mixed-type corrosion inhibitor. The adsorption of HAS on the mild steel surface obeyed the Langmuir adsorption isotherm. This was supported by the impedance measurements which showed a change in the charge transfer resistance and double layer capacitance, indicating the adsorption of HAS on the mild steel surface.

Key words: Mild steel, electrochemical impedance spectroscopy, inhibition, piper nigrum L., essential oil.

Introduction

The use of inhibitor is one of the most practical methods for protecting against corrosion and it is becoming increasingly popular [1]. Most of the well-known acid inhibitors are organic compounds. It has been reported that many heterocyclic compounds containing hetero atoms like N, O, S, have been proved to be effective inhibitor for the corrosion of mild steel in acid media [2]. The efficiency of corrosion inhibitors depends on the mechanical, structural and chemical properties of the layer formed. Inhibitors decrease the corrosion rate by adsorbing on the metal surface and blocking the active sites by displacing water molecules and form a compact barrier film on the metal surface. The efficiency of corrosion inhibitors are, among other factors, expensive and highly toxic, there is a growing interest in the use of natural products and environment friendly corrosion inhibitors, so-called "green inhibitors" such as leaves or seeds extracts.

Some papers have reported the use of natural products for mild steel corrosion inhibition in different environments [3-11]. Plant extracts are environment friendly, biodegradable, non-toxic, easily available and of potentially low cost. Most of the naturally occurring substances are safe and can be extracted by simple procedure. In the recent literature different extracts from many of the natural resources, such as, olive [12], henna [13], black pepper [14] and jojaba [15], oils extracted from different parts have proved their inhibitive ability towards metal corrosion in different aggressive media.

The aim of the present study is to investigate the corrosion inhibition effect of mild steel in 1 M HCl by the essential oils extracted from seeds of *Piper Nigrum* L. using weight loss, potentiodynamic polarization method and electrochemical impedance spectroscopy measurements at different concentrations at 308 K, after 6 h as immersion time. In this work, we tested essential oil obtained by three techniques: classical hydrodistillation and by microwave hydrodistillation on low and high microwave power.

2. Expérimental

2.1. Extraction of essential oils

The plant material was purchased from a supermarket and identified by Prof. M. Ramdani (Faculty of Sciences, Oujda, Morocco). In our previous work, [16] essential oils were isolated from seeds of *Piper Nigrum L*. by classical hydrodistillation (CHD) and microwave-assisted hydrodistillation (MHD) in yields of 1.24% and 1.45%, respectively. In both technique we used 25 g of seeds of black pepper Grinded, pulverized and subjected to steam distillation in water using a Clevenger type apparatus 1.5 h for (CHD) and 0.5 h for (MHD).



Fig.1: Seeds of *Piper Nigrum* L.

2.2. Analysis of essential oils

Essential oil composition was determined by gas chromatography coupled to mass spectrometry (GC-MS) analysis on a *Trace GC ULTRA* gas chromatograph coupled to a *Polaris Q MS* ion trap mass spectrometer. The column was VB-5 (Methylpolysiloxane, 5% phenyl), 30 m x 0.25 mm x 0.25 μ m film thickness with helium as carrier gas. Injection was performed at 220°C in the split mode; 1 μ L of sample was injected. GC oven temperature was kept at 40°C for 2min and programmed to 180°C at a rate of 4°C/min and increased to 300°C at a rate of 20°C/min then kept constant at 300°C for 2min. The MS operating parameters were as follows: ionization potential, 70 eV; ionization current, 2 A; ion source temperature, 200°C, resolution, 1000. Mass units were monitored from 30 to 450 m/z. The components of the oils were identified by comparison of the mass spectra fragmentation patterns with those found in databases or libraries (NIST02 [39], Adams [40], Wiley [41]).

2.3. Mild steel material

The mild steel (MS) specimens of composition (wt%): Fe: 99.21%; C: 0.21%; Si: 0.38%; P: 0.08%; Mn: 0.05%; S: 0.05%; Al: 0.01%, were used for electrochemical studies. Samples with sizes of 1cm x 1cm x 0.1cm cut in SS sheet were prepared by grinding each side with 180, 400, 600, 800, 1000, and 1200, grid emery paper and degreasing the surfaces ultrasonically with ethanol and finally dried in open air. All reagents used for the study were of analar grade and the solutions were prepared using double distilled water.

The aggressive solution used was made of AR grade HCl. A 1M solution of the acid was prepared using bidistilled water. The different concentrations of the oils were prepared (0.018; 0.037; 0.075; 0.15; 0.3 and 0.6g/L) in 100ml of 1M HCl.

2.4. Gravimetric Method

For weight loss measurements, pre-cleaned specimens were dipped in 100 mL of 1 mol L^{-1} HCl with and without the inhibitor maintained in a thermostated chamber at 308 ±1 K. Weight loss measurement was determined by retrieving the coupons after 6 hours of immersion. Triplicate specimens were used and the mean

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weight losses were reported. The difference in weight was taken as the weight loss of mild steel. The inhibition efficiency of the inhibitor, E%, the degree of surface coverage, θ , and the corrosion rate the mild steel were calculated using the following equations respectively:

$$E(\%) = \left(1 - \frac{W_1}{W_0}\right) \cdot 100 \text{ and } \theta = \frac{E(\%)}{100}$$
 (1)

Where, W_0 and W_1 are the weight losses (in g) for mild steel in the absence and the presence of the inhibitor in 1 M HCl solution, respectively.

2.5. Electrochemical measurements

Polarization experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. The working electrode (WE) was in the form of a square cut from mild steel with exposed surface area 1cm². Before measurement, the working electrode was polished mechanically, washed with acetone, rinsed several times with bidistilled water and dried. The freshly polished electrode was immersed in test solution at open circuit potential for 30 min until a steady state was reached. The polarization curve was recorded by polarization from -800 mV to -200 mV under potentiodynamic conditions corresponding to 1mV/s (sweep rate) and under air atmosphere. The corrosion inhibition efficiency E (%) was evaluated from the measured Icorr values obtained from Tafel polarization method using the relationship [32]:

$$E\% = \frac{I_{corr}^{\circ} - I_{corr}}{I_{corr}^{\circ}} \ge 100 \qquad (2)$$

Where I_{corr}° and I_{corr} are the corrosion current densities without and with the addition of various concentration of the inhibitor at 308K.

The potentiodynamic measurements were carried out using a VoltaLab100 electrochemical analyzer, which was controlled by a personal computer. AC impedance studies were also carried out in a three-electrode cell assembly. The data were analyzed using Voltamaster 4.0 software. The electrochemical impedance spectra (EIS) were aquired in the frequency range 100 kHz to 10 mHz at the free corrosion potential. The charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were determined from Nyquist plots. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility. All electrochemical studies were carried out with an immersion time of 1 h, with different inhibitory concentrations of essential oil and extract of Pelargonium, at 308 K. The inhibition efficiency (η %) of the inhibitor can be calculated from the charge transfer resistance values using the following equation:

$$E\% = \frac{R_{ct} - R_{ct}^{\circ}}{R_{ct}^{\circ}} \times 100$$
 (3)

Where, R°_{ct} and R_{ct} are the charge transfer resistance in the absence and in presence of inhibitors, respectively.

3. Results and discussions

3.1. Essential oils chemical composition:

The chemical composition of essential oils was given in table 1. Results showed that in the CHD extraction oil, β -caryophyllene as sesquiterpene hydrocarbon was the major compound present with 49.80%. MWHP extraction oil realized at a high microwave power (700W) was also rich in β -caryophyllene with relatively the same amount 52.67%. However, at low power 280W, the oxygenated compound caryophyllene oxide was selectively extracted with a high amount 63.13% because of his strongly microwave absorption [16]. In the case, β -caryophyllene as non polar compound presented a lower percentage 8.25%.

3.2. Weight loss measurements

The inhibitive effect can be explained on the basis of a mechanism suggesting adsorption of the oil on the surface of the metal which in turns acts as a film forming species decreasing the active area available for acid (HCl) attack [17].

Relative amount (%)						
		Microwave extraction ^(b)		Classical extraction		
		MWLP	MWHP	CHD		
Compounds	RT ^(a)	280w	700w			
Sabinene	9.11	-	3.01	5.76		
α-copaene	22.92	5.95	8.86	7.89		
Germacrene-D	23.39	1.13	1.83	1.68		
Caryophyllene	24.32	8.25	52.67	49.80		
α-Humulene	25.30	0.72	4.00	3.86		
Cubenol	27.20	3.85	5.10	5.20		
Caryophyllene oxide	29.08	63.13	4.79	2.46		

Table 1: Composition of major Microwave and Classical essential oils compounds extraction.

(a) Retention time in GC analysis.

(b) Microwave power used in microwave hydrodistillation of essential oils.

	E(%)					
Concentration g/l	CHD	Ecart type	MWLP	Ecart type	MWHP	Ecart type
0.02	58.22	1,327	56.35	4,705	57.22	3,424
0.04	62.76	3,230	60.76	2,599	60.76	2,677
0.08	67.6	2,375	66.36	5,439	64.61	3,667
0.15	73.2	3,611	73.82	8,739	70.82	1,004
0.3	78.36	4,536	81.23	5,760	75.63	4,182
0.6	85.65	5,562	90.6	4,069	83.46	3,444

It is clear from table 2 that these oils have good corrosion inhibition efficiency, but the important remark is that the efficiency of the oil obtained by the microwave technology at low power (MWLP) is the best. From the table 1, it can be seen that caryophyllene oxide (oxygenated compound) was a major compound by MWLP against the other two oils. So we can say that the MWLP oil is richer in polar compounds, such as heteroatoms which are responsible for the inhibition of corrosion, which explains the high efficiency of the MWLP comparing to CHD and MWHP [18-20].

3.3. Electrochemical impedance measurements

Electrochemical impedance measurements were carried out over the frequency ranging from 100 kHz to 10 mHz at open circuit potential. Nyquist plots for mild steel corrosion in 1 mol/L of HCl in the absence and the presence of various concentrations of oils obtained by different methods MWLP, CHD and MWHP are given in figures 2, 3 and 4 respectively. The inhibition efficiency, EI%, was evaluated from the measured charge transfer resistance values.

The locus of the Nyquist plots was regarded as one part of a semicircle. Nyquist plots of mild steel in inhibited and uninhibited acidic solution containing various concentrations of MWLP, CHD and MWHP are shown in figures 2, 3 and 4. The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion [21-27].

The deduced parameters such as charge transfer Resistance (Rct), inhibition efficiencies (EI%) of mild steel in 1 mol/L of HCl containing various concentrations of MWLP, CHD and MWHP oils are presented in table 3. The charge transfer resistance, Rt values are calculated from the difference in impedance at lower and higher frequencies [26,27]. To obtain the double capacitance (Cdl), the frequency at which the imaginary component of the impedance is maximum (- Z_{max}) is found and Cdl values are obtained from the following equation [28-30]:

$$f(-Zmax) = \frac{1}{2\pi C_{dl}R_{t}}$$
 (4)

The impedance parameters derived from these investigations are given in table 3. It is found that, as the inhibitor concentrations increases, the Rt values increase, but the C_{dl} values tend to decrease. The decrease in the C_{dl}

values is due to the adsorption of inhibitor on the metal surface. The better performance of MWLP in 1M HCl can be explained in the following way.

The inhibitor may be adsorbed on the metal surface in the form of polar molecules involving the deplacement of water molecules from the metal surface and sharing of electrons between the heteroatom or heterocyclic and the metal surface [23-26] may also be adsorbed through electrostatic interactions.

Being specifically adsorbed, they create a layer of excess negative charge directed towards the solution and favor more adsorption of the cations [8-10]. Strong adsorption of organic molecules is not always a direct binding of the molecule with the metal surface. The molecular compounds are important in synergistic inhibition.

Table 3: Electrochemical impedance parameter of MwLP, CHD and MwHP.						
inhibitors	Concentration	R _s	R _{ct}	C_{dl}	f (-Z _{max})	E
	(g/L)	$\Omega.cm^2$	$\Omega.cm^2$	(µF/cm ²)	(Hz)	(%)
	Blank	1.752	11.62	273.8	50,05	-
	0.018	1.728	75.23	66.84	31,67	84.55
	0.037	3	96.44	66	25,02	87.95
	0.075	1.901	115.6	55.02	25,04	89.95
	0.15	1.796	119.4	66.61	20,02	90.27
-	0.3	1.98	122.2	52.09	25.02	90.49
-	0.6	5.34	290.1	43.88	12.51	95.99
-	0.018	2.192	93.69	67.94	25,02	87.60
	0.037	2.187	97.67	65.17	25,02	88.10
	0.075	2.516	118.5	60.13	22,35	90.19
CHD -	0.15	2.461	129	49.32	25,03	90.99
-	0.3	2.153	140.2	56.72	20,02	91.71
-	0.6	2.365	142.8	55.69	20,02	91.86
	0,018	2,107	60,95	65,27	40,03	80,94
- MWHP - -	0,037	2,398	70,08	56,77	40,02	83,42
	0,075	2,232	81,94	61,37	31,67	85,82
	0,15	2,354	85,77	58,63	31,67	86,45
	0,3	2,3	94,82	53,03	31,68	87,75
	0,6	1,5	112,6	44,64	31.68	89,68



Fig. 2: Nyquist plots for mild steel corrosion in 1M HCl in the absence and the presence of various concentrations of MWLP.



Fig. 3: Nyquist plots for mild steel corrosion in 1M HCl in the absence and the presence of various concentrations of CHD.

Fig. 4: Nyquist plots for mild steel corrosion in 1M HCl in the absence and the presence of various concentrations of MWHP.

The Bode and phase angle plots recorded for mild steel electrode immersed in 1 M HCl in the absence and presence of optimum concentration of inhibitors are given in Fig. 5. It is observed that in the intermediate frequency region, a linear relationship between |Z| vs. *f* (Frequency) with a slope near -1 and the phase angle approaching -70° has been observed. This indicates the capacitive behavior at intermediate frequencies. An ideal capacitive behavior would be the result if a slope value attained -1 and a phase angle value attained -90° [33].

Fig. 5 Bode and Phase angle plots of mild steel in 1 M HCl in the absence and presence of different concentrations of MWLP, CHD and MWHP at 308K.

The phase angle plots (Fig.5) show single maximum (one time constant) at intermediate frequencies, broadening of this maximum in the presence of inhibitors (MWLP, CHD and MWHP) accounts for the formation of a protective layer on the electrode surface. All the impedance parameters were calculated using the application of the equivalent circuit model given in Fig. 7. A representative simulation of Nyquist diagrams with the suggested model in the case of MWLP, CHD and MWHP was given in Fig. 6.

Fig. 6. Simulation of Nyquist diagrams with suggested model for MWLP, CHD and MWHP at 0.6 g par L.

The circuit consists of Rs (the resistance of the solution between working electrode and the counter electrode) and Rct (The difference in real impedance at lower and higher frequencies is commonly considered as charge transfer resistance.). The double layer usually behaves as a constant phase element (CPE) rather than pure capacitor.

Fig.7. Equivalent circuit used to fit the impedance spectra of Essential Oils Extracted (MWLP, CHD, and MWHP).

3.4. Electrochemical measurements

The nature of the inhibition process has been established on the basis of polarisation measurements. Figures 8, 9 and 10, represent the kinetics of the anodic and cathodic reactions occurring on mild steel electrodes in 1M HCl solutions without and with different concentrations of MWLP, CHD and MWHP oils at 308K respectively. The corrosion inhibition efficiency E (%) was evaluated from the measured Icorr values obtained from Tafel polarisation method using the relationship (2).Values of all electrochemical corrosion kinetic parameters such as corrosion potential (Ecorr), cathodic and anodic Tafel slopes (βc , βa) and corrosion current density (Icorr) attained by extrapolation of Tafel lines, as well as inhibitor efficiency are listed in Table 4.

Table 4: Polarization parameters and corresponding inhibition efficiency for the corrosion of the mild steel in 1M HCl without and with addition of various concentrations of MWLP; CHD and MWHP at 308 K

Inhibitors	C g/L	E _{corr} mV/ECS	-β _c mV/dec	β _a mV/dec	I _{corr} μA/cm ²	E (%)
	blank	-460.9	141.6	133.9	1941.9	-
MWLP	0.018	-465.9	244.4	144	636.7	67.21
	0.037	-462.4	193.5	111.9	451.7	76.74
	0.075	-480.3	192.4	116.4	386.4	80.10
	0.15	-476.9	214	114	335.8	82.71
	0.3	-476.3	207.6	108.1	326.2	83.20
	0,6	-465.4	77.5	82.7	96.7	95.02
CHD	0.018	-461	241.4	132	739.3	61.93
	0.037	-468.3	229.4	131	656.2	66.21
	0.075	-446.8	237.5	114.8	520.5	73.20
	0.15	-461.3	245.8	123.6	519.7	73.24
	0.3	-448.5	232.2	112.9	476.2	75.48
	0.6	-449.1	225	104.4	351.4	81.90
МШНР	0.018	-466.6	235.6	137.4	864.9	55.46
	0.037	-456.5	220.8	126.5	775.1	60.09
	0.075	-462.9	206.4	129.2	702.4	63.83
	0.15	-454.5	215.6	120.8	691.4	64.40
	0.3	-477.4	220.1	113.5	442.3	77.22
	0.6	-469.8	87.3	91	237.6	87.76

From Fig. 8, 9 and 10, it is clear that both the anodic metal dissolution and cathodic hydrogen evolution reactions were inhibited after the addition of MWLP, CHD and MWHP inhibitors to the aggressive medium. The inhibitions of these reactions are more pronounced with the increasing inhibitor concentration while the corrosion potential values shifted slightly to more positive direction. Therefore, it could be concluded that MWLP, CHD and MWHP can be classified as mixed type inhibitors but dominantly act as an anodic inhibitor at high concentration for mild steel in 1M HCl.

Example, the decrease in current density with increasing of the concentration of MWLP indicates that this compound is adsorbed on the metal surface and hence inhibition occurs.

This can be explained on the basis that adsorbed inhibitor may form a surface film which acts as a physical barrier to restrict diffusion of ions to or from the electrode surface, and hence retard the corrosion process. Further inspection of figure 10 reveals that Cathodic current potential curves give rise to parallel Tafel lines indicates that the hydrogen evolution reaction is activation-controlled and the reduction of H⁺ ions at the mild steel surface occur mainly through a charge transfer mechanism. In agreement with the numerous studies in the literature [31, 32] the inhibiting action of the plant extract was due to the adsorption of their organic compounds

onto the metal surface, and/or by covering the surface with layers of their complex or chelate precipitate with metal ions.

The inhibition performance of the plant extract applied in this study is ascribed to the presence in its various compositions of complex organic species, which contained several sites (such as sulphur, nitrogen, and oxygen) and/or aromatic ring in their molecular structure that could act as centres for its adsorption on the mild steel surface [19-23].

Fig. 8: Polarization Curves mild steel in a 1M HCl with and without different concentrations of MWLP.

Fig. 9: Polarization Curves mild steel in a 1M HCl with and without different concentrations of CHD

Fig. 10: Polarization Curves mild steel in a 1M HCl with and without different concentrations of MWHP.

The results of the inhibition efficiencies obtained from weight loss measurements, potentiodynamic polarization curves and EIS are in good reasonably agreement.

3.5 Adsorption Isotherm

Inhibition effects are based on the adsorption of molecules onto the metal surface to form an impermeable protective film and shielding it from the corrosive media. On the other hand, the adsorbed molecules can combine with the oxide layer on the metal (rust deposited) and react chemically to produce a more protective surface network by changing the film structure. The adsorption mechanism of organic compounds occurs either directly, on the basis of donor– acceptor interactions between the relatively loosely bound electrons such as in anions and organic molecules and/or the heterocyclic compound which has lone pair electrons, or the π -electrons with the vacant d-orbitals of metallic iron atoms. Some parameters such as organic molecule size, number of functional groups, polarity that contribute to the formation of a strong bond or the rate of adsorption of inhibitor compounds onto the surface could affect the adsorption mechanism or inhibition action [34].

The Langmuir adsorption isotherm provides a simple mechanistic picture of the adsorption process and gives rise to a relatively simple mathematical expression. The Langmuir adsorption isotherm may be written in the following rearranged form [35]:

$$\frac{C}{\theta} = C + \frac{1}{K} \tag{5}$$

Where C is the concentration of inhibitor, K is the adsorptive equilibrium constant, θ is the surface coverage. The surface coverage θ , was determined using the following equation:

$$\theta = \frac{\mathrm{E}(\%)}{100} \tag{6}$$

For all the three extracted (MWLP, CHD, and MWHP) used in this study (weight loss), a plot of C/ θ against C gave straight lines with the slope of unit (Fig. 11). This means that the adsorption of the Piper Nigrum L. Essential oils **e**xtract on the mild steel surface obeys the Langmuir isotherm.

Table 5: The values of free Gibs energy of adsorption calculated using the results of study method Weight loss.

inhibitor	K _{ads} L mol ⁻¹	Linear coefficient regression (r)
CHD	41.8935903	0.99902
MWLP	33.3333333	0.99838
MWHP	38.7897595	0.99875

The calculated values are given in Table 5.

Fig. 11: Langmuir isotherm for the adsorption of MWLP, CHD, and MWHP on the mild steel surface.

Conclusion

The study of effect of *piper nigrum* essential oil on the corrosion of mild steel in molar HCl conducted by weight loss, potentiodynamic polarization method and electrochemical impedance spectroscopy measurements may draw the following conclusions:

- 1- Results have shown that essential oils extracted by classical or microwave hydrodistillation acted as good inhibitors, and the inhibition efficiency increased with increase in concentration of inhibitors for 0.018 g/L to 0.6 g/L at 306K after 6h as immersion time.
- 2- The maximum inhibition efficiency (95.99%) was found for the microwave essential oil on low microwave power at 0.6g/L at 308 K, after 6 h as immersion time. However, the essential oils extracted by classical hydrodistillation and by microwave method on high microwave power presented relatively a low performance (91.86% and 89.68%) as inhibition efficiency respectively. The difference of the results was in good concordance with the chemical composition of the three amounts of essential oils.
- **3-** The inhibition of the corrosion of mild steel in 1 M HCl by the essential oils of *piper nigrum* is due to the phytochemical constituents of the extract.
- 4- The polarization measurements show that the oils of *piper nigrum* L. act as an inhibitor of mixed type and impedance method indicates that the oils adsorb on the mild steel surface with increasing transfer resistance and reducing the double layer capacitance.
- **5** The inhibitory effectiveness determined by electrochemical polarization, electrochemical impedance spectroscopy and by gravimetric methods are generally in good agreement.
- **6-** In view of the findings, it may be concluded that the essential oils of *piper nigrum* fruit can be considered as a source of relatively cheap, eco-friendly and effective acid corrosion inhibitor.

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