

COPPER CORROSION BEHAVIOR IN PHOSPHORIC ACID CONTAINING CHLORIDE AND ITS INHIBITION BY ARTEMISIA OIL

F. Mounir¹, S. El Issami¹, Lh. Bazzi³, R. Salghi², L. Bammou¹, L. Bazzi^{1*}, A. Chihab Eddine⁴ & O. Jbara⁵

¹Laboratoire Matériaux et Environnement, Faculté des Sciences d'Agadir. Morocco.

²Equipe de Génie de l'Environnement et de Biotechnologie, ENSA, Agadir, Morocco.

³Etablissement Autonome de Contrôle et de Coordination des Exportations Agadir. Morocco.

⁴Laboratoire Chimie Organique, Faculté des Sciences d'Agadir. Morocco.

⁵GRSPI, Equipe Matériaux Fonctionnels, Université de Reims.

*Email: l.bazzi@uiz.ac.ma

ABSTRACT

Corrosion behaviour of copper in phosphoric acid containing sodium chloride at different concentrations was studied in the first part of this paper to illustrate the aggressiveness of chloride toward copper corrosion in this medium. The second part treated copper corrosion inhibition effect of Artemisia oil (AO) extracted from Artemisia herbaalba. Three experimental techniques have been used such as weight-loss, electrochemical polarization measurements and electrochemical impedance spectroscopy (EIS).

The result obtained shows that corrosion rate of copper in phosphoric acid increases with increasing chloride concentration from 10^{-3} to 3.10^{-1} M. The inhibitory effect of Artemisia oil (AO) was then studied in more aggressive medium (2 M H_3PO_4 + 3.10^{-1} M NaCl) at different temperatures. The results obtained show that AO is a good inhibitor. The naturally oil reduces effectively the corrosion rate of copper. The inhibition efficiency was found to increase with oil content to attain 89% at 6 g/l. AO acts as a mixed inhibitor. The effect of temperature on copper corrosion indicates that inhibition efficiency of the natural substance decreases with the rise of temperature. Inhibition efficiency values obtained from weight loss, polarization curves and EIS are in reasonably good agreement.

Keywords: Corrosion; inhibition; Artemisia oil; copper; phosphoric acid; Chloride.

1. INTRODUCTION

The use of inhibitors is one of the most practical methods to secure metals against acid corrosion. Phosphoric acid is produced in large quantities in Morocco. It is widely used in industries, for example, in the food industry, acid pickling, acid cleaning and acid desalting. It is not very corrosive compared to nitric or sulfuric acids. Nowadays, 95% of the Phosphoric acid is obtained by wet process: phosphate rocks are attacked by sulfuric acid. This technique generates severe corrosion problems caused by the presence of impurities such as chlorides, fluorides and sulfides in the hot phosphoric acid and by erosion phenomena [1–10].

Copper is used widely in industry, because of its good thermal conductivity and mechanical properties. Copper is a relatively noble metal. Nevertheless, it reacts easily in ordinary environments containing oxygen. Thus, the study of its corrosion inhibition has attracted much attention. Copper corrosion depends not only on the nature of the environment but also of the condition of use on materials. Most work on copper corrosion reveals that the presence of aggressive elements such as chloride and sulfide accelerates the corrosion of this metal [11–13]. One of the most important methods in the corrosion protection of copper is the use of organic inhibitors [14–15]. These last decades, researches are reoriented to the application of non-toxic inhibitors called green or eco-friendly environment inhibitors. Natural plants were added in form of extracts, oil or pure compounds, may play major role to keep the environment more healthy, safely and under pollution control. Among the various natural products, we cite Lawsonia extract [16], Hibiscus Sabdariffa extract [17], Garcinia kola extract [18], fenugreek extracts [19], Phyllanthus amarus extract [20], eucalyptus oil [21, 22], azadiracta indica [23], black pepper [24], etc. have been reported to be good inhibitors for copper in acidic solutions.

In our laboratory, several oils of natural plants were tested and may be used as efficient inhibitors such as Argania spinosa [25], Artemisia oil [26], Thymus satureioides essential oils [27] and Prickly pear seed oil extract [28].

This work is devoted to examining the corrosion action of NaCl in 2M H_3PO_4 and to study the Artemisia oil (AO) leaves as green inhibitor for corrosion of copper in 2 M H_3PO_4 solution containing 3.10^{-1} M NaCl. Weight loss measurements, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) techniques were used in this study.

2. EXPERIMENTAL METHODS

2.1. Artemisia oil (AO)

Artemisia herbaalba was collected in the region of Agadir, Morocco. It was taxonomically identified at the National Scientific Institute of Rabat (Department of Plant Biology, Laboratory of Botany). A voucher specimen of sample was deposited in the Herbarium of the Laboratory of the science faculty Ibn Zohr University, Agadir Morocco. The aerial parts of

the plant were air-dried in the laboratory at room temperature. A sample of 200 g was subjected to water distillation for 2h using a Clevenger-type apparatus recommended by the French Pharmacopoeia [29]. The yield was determined as grams over the 200 g of powder analysed in percentage, and are shown in Table 1.

The oil was analyzed using a Hewlett-Packard 5972 MS, fitted with a HP 5890 Series II GC and controlled by a G1034C Chemstation. A sample of 1 μ L was injected under the following conditions: DB-1 fused silica capillary column (20 m x 0.20 mm, film thickness 0.2 μ m); carrier gas helium (0.6 mL/min); injector temperature 250 °C; column temperature 50-250°C at 3°C/min; MS electronic impact 70 eV. The identification of the compounds was achieved by comparing retention times and mass spectra with those of the published standards [30, 31].

2.2. Weight loss measurements

Gravimetric methods were conducted on copper test samples of a Total surface of 12 cm². All experiments were carried out under total immersion in 75 ml of test solutions. Mass loss was recorded by an Analytical balance. Prior to each gravimetric or electrochemical experiment, the surface of the specimens was polished successively with emery paper up to 1200 grade, rinsed thoroughly with acetone and distilled water before plunging the electrode in the solution. Pure copper samples (99%) were used. The experiments were carried out in 2 M H₃PO₄ medium containing different concentration of NaCl; it was prepared by dilution of Analytical Grade 84% H₃PO₄ with distilled water and pure NaCl.

2.3. Electrochemical tests

The current–voltage characteristics are recorded with a potentiostat PGP 201, controlled by a computer. The scan rate is 30mV/min and the potential is ranged from cathodic to anodic potentials. Before recording each curve, the working electrode is maintained with its free potential of corrosion E_{corr} for 30 min. The polarisation curves are obtained from –800 mV to 500 mV at 293K. We used for all electrochemical tests a cell with three electrodes and double wall thermostats (Tacussel Standard CEC/TH). Saturated calomel (SCE) and platinum electrodes are used as reference and auxiliary electrodes, respectively.

The working electrode is in the form of a disc from pure copper of the surface 1 cm².

The tests were carried out in a temperature range 293–323K. The electrochemical impedance spectroscopy (EIS) measurements are realised with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at E_{corr} after 30 min immersion in solution. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure at 293 K. The impedance diagrams are given in the Nyquist representation.


Experiments are repeated three times to ensure the reproducibility.

3. RESULTS AND DISCUSSION

3.1. Artemisia oil (AO) analysis

GC-mass spectrum analyzes permit the identification of the composition of *Artemisia* essential oil. The main components are listed in table 1. AO mainly contains camphor, α -thuyone, β -thuyone, camphene and 1,8-cineole (table 2).

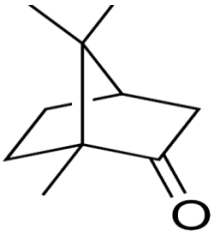
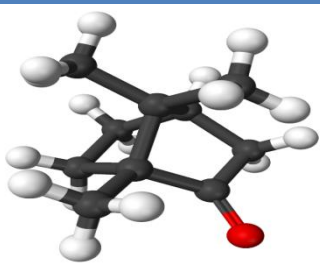
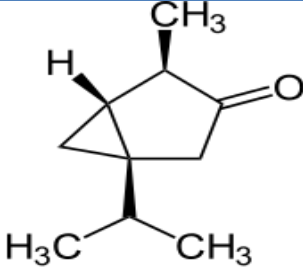
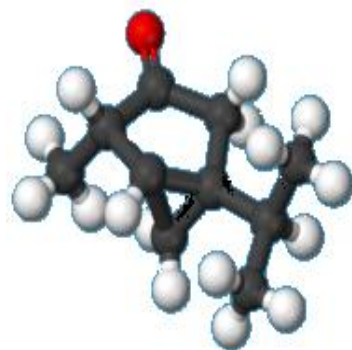
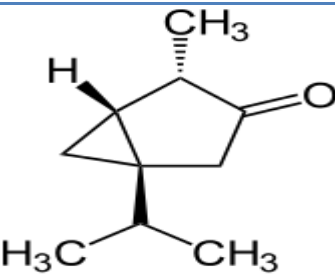
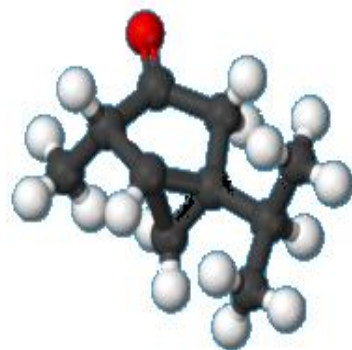
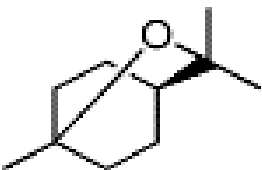
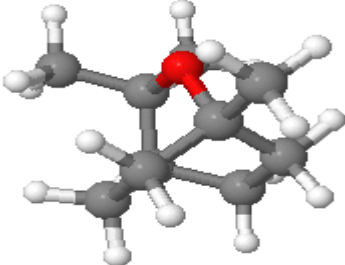
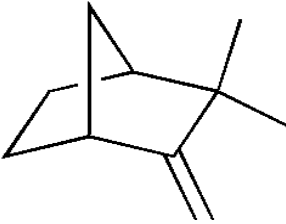
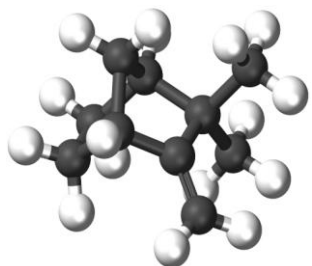
Table 1. Chemical composition of Artemisia essential oils.

Plant species	Family	Yield (%) ^a	Major constituents	(%) ^b
	Asteracées	1.5	Camphor, (C ₁₀ H ₁₆ O)	46.0
			α -thuyone, (C ₁₀ H ₁₆ O)	33.2
			β -thuyone, (C ₁₀ H ₁₆ O)	09.0
			1,8-cineole, (C ₁₀ H ₁₈ O)	06.4
			Camphene, (C ₁₀ H ₁₆)	08.5

^aGrams of extracted oil as percentage over the 100 g of powder analyzed.

^bGrams over total extracted oil in percentage

Table 2. The systematic (IUPAC) name, 2D and 3D chemical structure of the main constituents of Artemisia oil

The constituent	The systematic (IUPAC) name	The 2D chemical structure	The 3D chemical structure
Camphor	1,7,7Trimethylbicyclo[2.2.1]heptan-2-one.		
α -thuyone	(1 <i>S</i> ,4 <i>R</i> ,5 <i>R</i>)-4-Methyl-1-(propan-2-yl)bicyclo[3.1.0]hexan-3-one.		
β -thuyone	(1 <i>S</i> ,4 <i>S</i> ,5 <i>R</i>)-4-methyl-1-propan-2-ylbicyclo[3.1.0]hexan-3-one		
1,8-cineole	1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane		
Camphene	2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane.		

3.2. Gravimetric measurement

Table (3) summarizes the gravimetric trends of the copper immersed in 2 M H₃PO₄ in absence and presence of NaCl at concentration varying from 10⁻³ to 3.10⁻¹ M.

Table 3. Effect of NaCl concentration on corrosion data of copper in 2 M H₃PO₄

Solution	x (mole.L ⁻¹)	W _{cor} (mg.j ⁻¹ .dm ⁻²)
2M H ₃ PO ₄ + xM NaCl	0	020
	10 ⁻³	028
	10 ⁻²	031
	10 ⁻¹	040
	2.10 ⁻¹	100
	3.10 ⁻¹	162

From results of table 3, it is clear that corrosion rate (W_{corr}) increase with increasing chloride concentration from 10⁻³ to 3. 10⁻¹ M of NaCl. Then, 2M phosphoric acid containing 3.10⁻¹ M NaCl was the more corrosive medium. So, the inhibitory effect of AO will be investigated in this electrolyte.

Table (4) gives the gravimetric parameters of the copper immersed in 2 M H₃PO₄ + 3.10⁻¹M NaCl in absence and presence of the inhibitors at various concentrations. In the same table, it summarizes Inhibition efficiency values E_w (%) of AO at different concentrations. We noted that E_w (%) was calculated as follows:

$$E_w (\%) = \frac{W_{\text{corr}} - W'_{\text{corr}}}{W_{\text{corr}}} \times 100 \quad (1)$$

where W_{corr} and W'_{corr} are the corrosion rate of copper in 2 M H₃PO₄ + 3.10⁻¹M NaCl in absence and presence of inhibitor.

Table 4. Effect of AO concentration on corrosion data of copper in (2 M H₃PO₄ + 0.3. M NaCl).

Solution	x (g/L)	W' (mg.j ⁻¹ .dm ⁻²)	E _w (%)
2M H ₃ PO ₄	0	162	-
+ 3.10 ⁻¹ M NaCl + x(g/l)A O	1	115	26
	2	088	43
	3	068	56
	4	051	67
	5	037	76
	6	020	87

It is clear that The corrosion rate W'_{corr} decreases with the increase of concentration of the tested inhibitors and in turn the inhibition efficiency (E_w%) increases to attain 87% at 6g/L of AO. From weight loss measurements, we can conclude that AO is a good inhibitor.

3.2.2 Polarization curves

Fig.1 shows polarization curves of copper obtained in 2M phosphoric acid with various concentrations of NaCl in the potential range from -0.6 to 0.5 V/SCE.

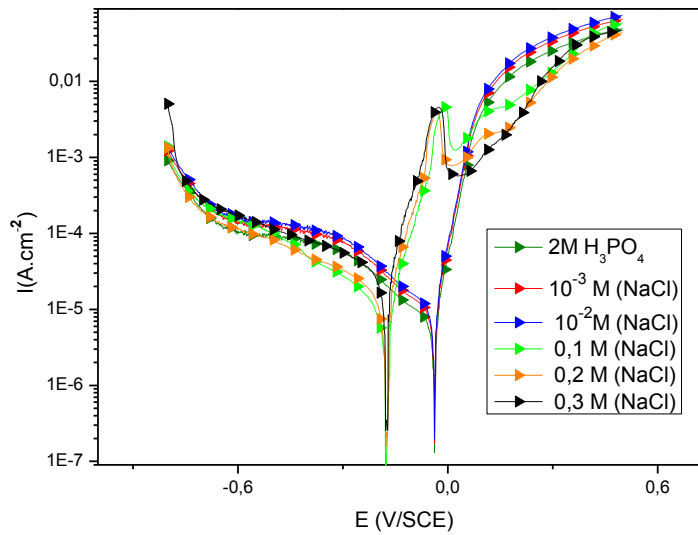
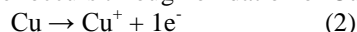
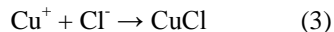


Fig. 1: Cathodic and Anodic polarisation curves of copper in 2M H₃PO₄ in the presence of NaCl at different concentrations.

The comparison of the curves shows that the behaviour of copper is a function of chloride concentration. All cathodic polarization curves are similar to cathodic one plotted in free chloride medium. They present a large linear domains characteristic of charge transfer mechanism [32]. However, the anodic polarization curves were more influenced by the presence of chloride ions in acid solution. Indeed, in chloride free solution, there are the Tafel region at lower over-potentials attributed to the dissolution reaction of Cu to Cu(I) [33]. For more anodic potential, anodic current density continues to increase but not linearly. This variation was assigned to the oxidation of Cu(I) to Cu(II) species [34]. The recorded polarization curve in the medium containing a concentration less than 0.1M NaCl is similar to that plotted in H₃PO₄ medium (Fig. 1). In the presence of chloride at concentration equal or superior of 10⁻¹M, anodic dissolution of copper occurs through oxidation of Cu(0) to Cu⁺ [35],



This Cu⁺ reacts with chloride ion from the solution and forms CuCl,



The formed CuCl has poor adhesion, is unable to protect the copper surface, and transforms to the soluble cuprous chloride complex, CuCl₂⁻ [36, 37],



here, three distinct regions can be identified for Cu in phosphoric acid medium containing chloride at concentration varying from 10⁻¹ to 3.10⁻¹M: a Tafel region at lower over-potentials extending to the peak current density due to the dissolution of copper into Cu⁺, Eq. (2); a region of decreasing currents until a minimum is reached due to formation of CuCl, Eq.(3); a region of sudden increase in current density as a result of CuCl₂⁻ formation, Eq.(4), which is the responsible on the dissolution of Cu [38].

The electrochemical parameters deduced from Figure 1 are summarized in Table 5.

Table 5. Electrochemical parameters of copper at various concentrations of NaCl in 2M H₃PO₄.

Milieu	x (M)	E _{corr} (mV/SCE)	I _{corr} (μA/cm ²)	b _a (mV/dec)	b _c (mV/dec)
	0	-039	06	57	-374
2M H ₃ PO ₄ + x M NaCl	10 ⁻³	-042	07	58	-330
	10 ⁻²	-040	9	57	-307
	10 ⁻¹	-177	11	56	-292
	2.10 ⁻¹	-176	20	57	-294
	3.10 ⁻¹	-177	36	68	-297

We note that the corrosion potential shifts to values more negatives when the chloride content in solution exceeds 10⁻¹M. Corrosion current density I_{corr} increases and reached a value of 36 μA/cm² at 3.10⁻¹M NaCl. These results are in good agreement with gravimetric tests.

Anodic and cathodic polarization curves of copper in (2M H₃PO₄ + 3.10⁻¹M NaCl) in absence and presence of various concentrations of AO at 20°C are shown in Fig. 2. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope (b_c), anodic Tafel slop (b_a) and inhibition efficiency (E%) are listed in Table 6. E% was calculated by the following equation:

$$E\% = \left(1 - \frac{I'_{corr}}{I_{corr}}\right) \times 100 \quad (5)$$

where I_{corr} and I'_{corr} are the corrosion current density values without and with the inhibitor, respectively, determined by extrapolation of the Tafel lines to the corrosion potential.

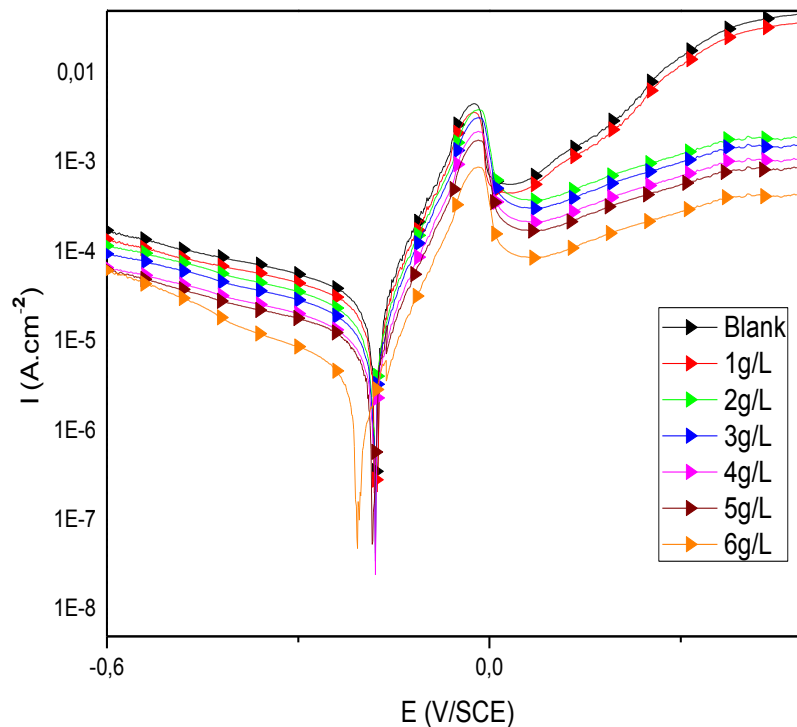


Figure 2. Cathodic and Anodic polarisation curves of copper in (2M H₃PO₄+ 3.10⁻¹M NaCl) in the presence of Artemisia oil at different concentrations.

Analysis of the polarization curves indicates that the presence of natural oil studied leads both to decrease the cathodic and anodic current densities. The anodic polarization curves of copper electrode in 2M H₃PO₄ + 3.10⁻¹M NaCl with AO present an important change. This effect is characterized by an important decrease of copper current dissolution. The anodic peak of the active zone decreased with increasing the AO concentration. This peak is followed by a passivity plateau. However, no significant change was observed for the corrosion potential in the presence of AO emphasizing that this oil compound act as a mixed type inhibitor.

All the electrochemical parameters deduced from Figure 2 are summarized in Table 6. We note that the corrosion current density decreases monotonically when the content of AO increases in solution. I_{corr} reaches a value 4 μA/cm² at a concentration of 6 g/l of the oil. This value of I_{corr} led to an inhibition efficiency of about 89% and confirms the AO inhibitor against the corrosion of copper in 2M H₃PO₄ medium containing 3.10⁻¹M NaCl. Note that the values of anodic and cathodic Tafel slopes are not much altered by the presence of AO. This result suggests that copper corrosion mechanism in the medium studied is not changed by the presence of the inhibitor. AO probably acts by a simple blocking of anodic and cathodic sites on the surface of copper.

Table 6. Electrochemical parameters of copper at various concentrations of OA in (2M H₃PO₄+ 0.3M NaCl) and the corresponding inhibition efficiency

Solution	x (g/l)	E _{corr} (mV/SCE)	I _{corr} (μA/cm ²)	b _a (mV/dec)	b _c (mV/dec)	Ei (%)
(2M H ₃ PO ₄ + 0.3 NaCl) + xM AO	0	-177	36	68	-297	-
	1	-177	25	67	-254	25
	2	-180	22	62	-235	39
	3	-180	18	62	-175	50
	4	-180	13	58	-111	64
	5	-180	10	57	-106	72
	6	-208	04	63	-255	89

3.3. Electrochemical impedance spectroscopy measurements

The corrosion behaviour of copper in 2M phosphoric acid solution in the presence and absence of NaCl, is also investigated by the electrochemical impedance spectroscopy (EIS). The measures were performed at 293 K after 30 min of immersion of the copper electrode in the corrosive environment. Fig. 3 shows the corresponding Niquist diagram. The impedance parameters derived from these investigations are mentioned in Table 7.

In all cases, the diagram shows a single Niquist capacitive loop. This result confirms that copper corrosion in the environment studied is governed by charge transfer mechanism.

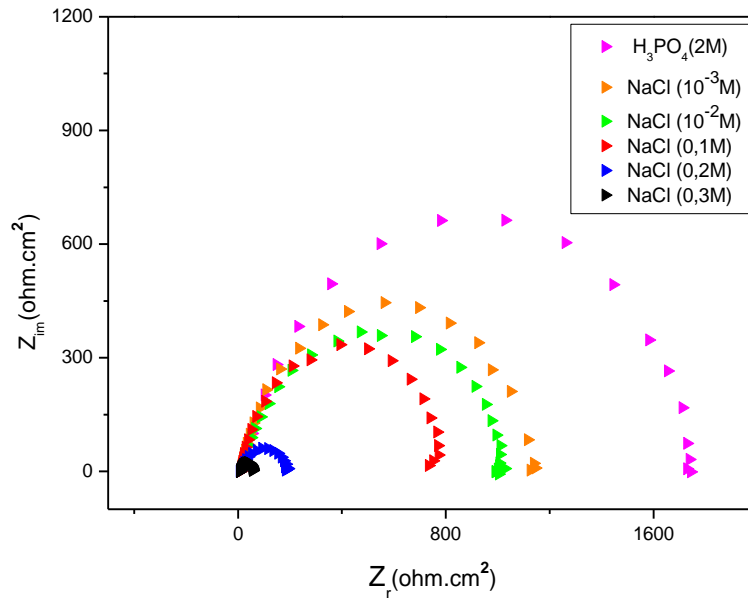


Figure 3. Nyquist diagrams for copper electrode with and without NaCl addition after 30min of immersion at E_{corr} .

Table 7. EIS parameters for copper corrosion in 2M H_3PO_4 acid at various contents of NaCl.

Inhibitors	x (M)	$R_t(\Omega.cm^2)$	$f_{max}(Hz)$	$C_{dl}(\mu F/cm^2)$
2M H_3PO_4 + x M NaCl	0	1760	02	41
	10^{-3}	1136	03	46
	10^{-2}	1038	05	31
	0.1	0793	07	29
	0.2	0189	18	47
	0.3	0051	63	50

Impedance measurements on the Cu electrode in a 2M H_3PO_4 + 0.3M NaCl solution and in the presence of varying inhibitors concentrations were performed at the open-circuit potentials after 30 min of immersion at E_{corr} . Fig.4 represents the influence of AO concentrations on Nyquist impedance spectra. At open circuit, the spectrum shows one capacitive loop. In the presence of AO, the capacitive loop size increases.

The double layer capacitance (C_{dl}) and the maximum-frequency capacitive loop (f_{max}) at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation:

$$C_{dl} = \left(\frac{1}{\omega \cdot R_t} \right)$$

with $\omega = 2\pi f_{max}$ (6)

where C_{dl} : Double layer capacitance ($\mu F.cm^2$); f_{max} : maximum frequency (Hz) and R_t : Charge transfer resistance ($\Omega.cm^2$).

The values of f_{max} , C_{dl} and the charge transfer resistances R_t were presented in Table 8. We can see that, the R_t value increases with increasing concentration of AO in 2M H_3PO_4 + 0.3M NaCl solution, whereas C_{dl} decreases. This suggests that the copper surface coverage increases with AO concentration. The capacitance value C_{dl} is about 50 $\mu F/cm^2$ in the absence of AO and 28 $\mu F/cm^2$ in the presence of AO at 6 g/L (Table 8). The decrease of the

capacitance can be explained by a reduction of the active metal surface, which is probably due to the species adsorption or to the development of compounds on the surface [39].

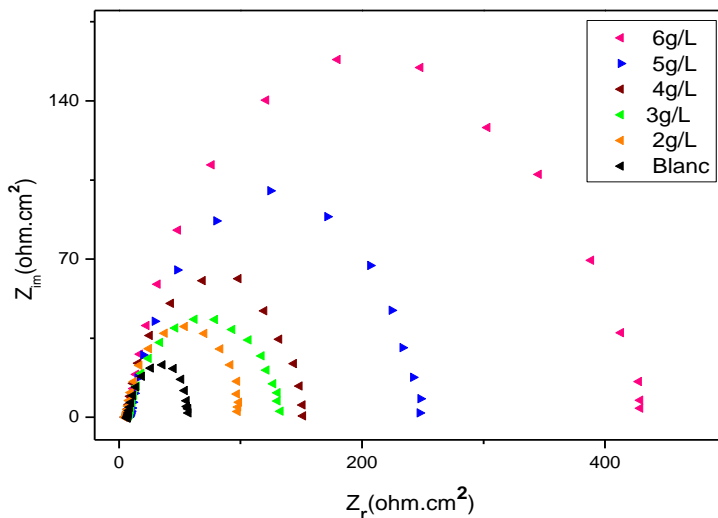


Figure 4. Nyquist diagrams for copper electrode in (2M H₃PO₄+ 0.3 NaCl) with and without OA after 30min of immersion at E_{corr}.

The values of inhibition efficiency were calculated using the relation:

$$E_{Rt} \% = \frac{(R_t - R_t^0)}{R_t} \times 100 \quad (7)$$

Where R_t and R_t⁰ are the charge transfer resistances in inhibited and uninhibited solutions respectively.

The charge transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [40].

It is worthy noting that the presence of inhibitors does not alter the profile of impedance diagrams which are almost semi-circular (Fig.4), indicating a charge transfer process mainly controls the corrosion of copper. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena [41, 42].

In Table 4, the homogeneous evolution of the inhibition efficiency, calculated from impedance spectra at free potential in the presence of AO at various concentrations, is presented. This inhibition efficiency increases when the inhibitor concentrations increase. Inhibition efficiency values exceed 87 % at 6 g/L of AO. This confirms the results obtained by potentiodynamic and gravimetric tests.

Table 8. Impedance parameters for corrosion of copper in (2M H₃PO₄+ 3.10⁻¹M NaCl) at various concentrations of AO.

Inhibitors	x (g/L)	R _t (Ω.cm ²)	f _{max} (Hz)	C _{dl} (μF/cm ²)	E _{RT} (%)
2M H ₃ PO ₄ + 0.3 NaCl + xM AO	0	51	63	50	-
	2	94	56	30	46
	3	126	50	25	59
	4	139	32	36	63
	5	236	22	31	78
	6	400	14	28	87

3.3. Effect of temperature

3.3.1. Polarization curves

Temperature has a great effect on the corrosion phenomenon. Generally the corrosion rate increases with the rise of the temperature. For this purpose, we made potentiodynamic polarization in the range of temperature 293 to 323 K, in the absence and presence of AO at 6g/L. The corresponding data are shown in fig 5, 6 and Table 9.

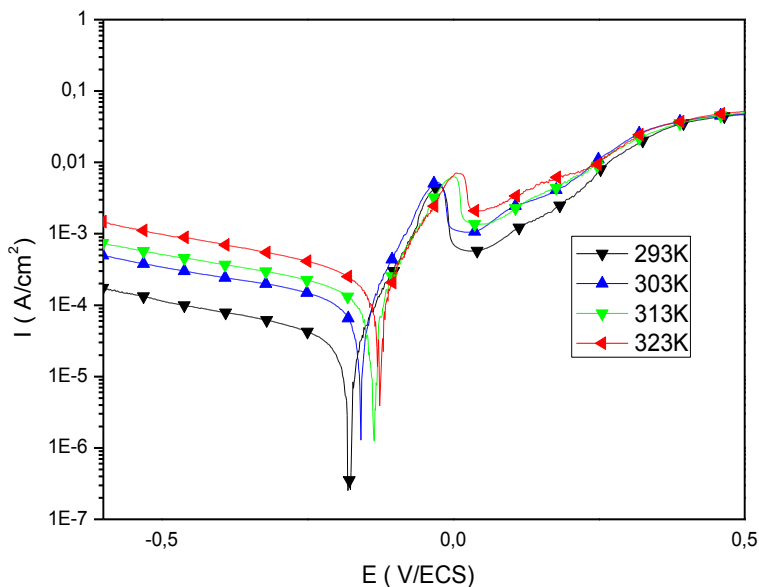


Figure. 5 Potentiodynamic polarisation curves of copper in (2M H₃PO₄ + 3.10⁻¹M NaCl) at different temperatures

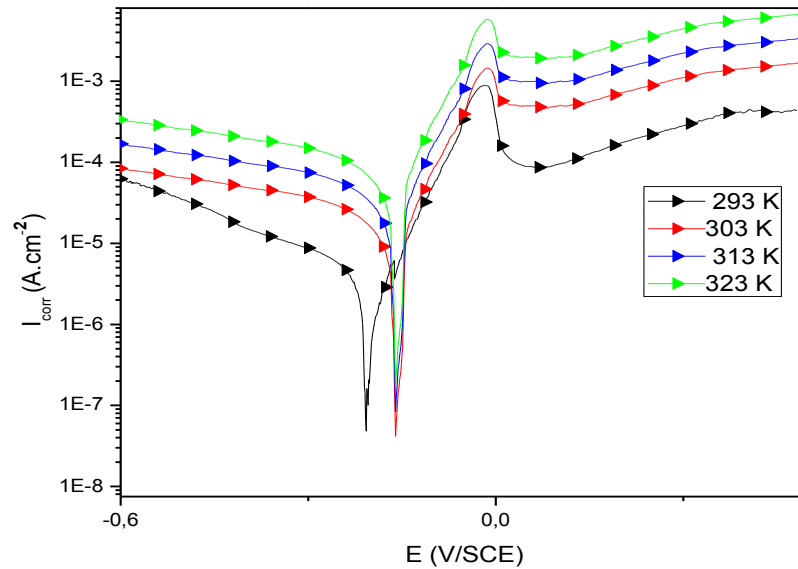


Figure.6 Potentiodynamic polarisation curves of copper in (2M H₃PO₄ + 3.10⁻¹M NaCl) at different temperatures

Table9. Effect of temperature on the copper in (2M H₃PO₄ + 0.3 M NaCl) and at 6g/L of AO.

Inhibitors	Temperature (K)	E _{corr} (mV/SCE)	I _{corr} (μA/cm ²)	b _a (mV/dec)	b _c (mV/dec)	E (%)
Blank	293	-177	036	68	-297	-
	303	-157	116	63	-516	-
	313	-136	174	54	-504	-
	323	-128	251	50	-355	-
Artimisia Oil	293	-208	004	63	-355	89
	303	-158	026	50	-453	77
	313	-158	050	35	-245	71
	323	-158	108	15	-065	57

It is clear from fig. 5 and table 9 that the increase of corrosion rate is more pronounced with the rise of temperature for blank solution.

As seen from fig. 6 and table 9 in the presence of AO, I_{corr} is highly reduced. Also, the inhibition efficiency decreases slightly with increasing temperature. This can be explained by the decrease of the strength of adsorption processes at elevated temperature and suggested a physical adsorption mode [43]. From this result, we can conclude that AO is a good inhibitor.

3.3.2. Kinetic parameters

The activation energies of corrosion process in free and inhibited acid were calculated using Arrhenius equation (8):

$$I_{\text{corr}} = A \exp\left(-\frac{E_a}{R.T}\right) \quad (8)$$

Where A is Arrhenius factor, E_a is the apparent activation corrosion energy, R is the perfect gas constant and T the absolute temperature.

Plotting (log I_{corr}) versus 1/T gives straight lines as revealed from Fig. 7.

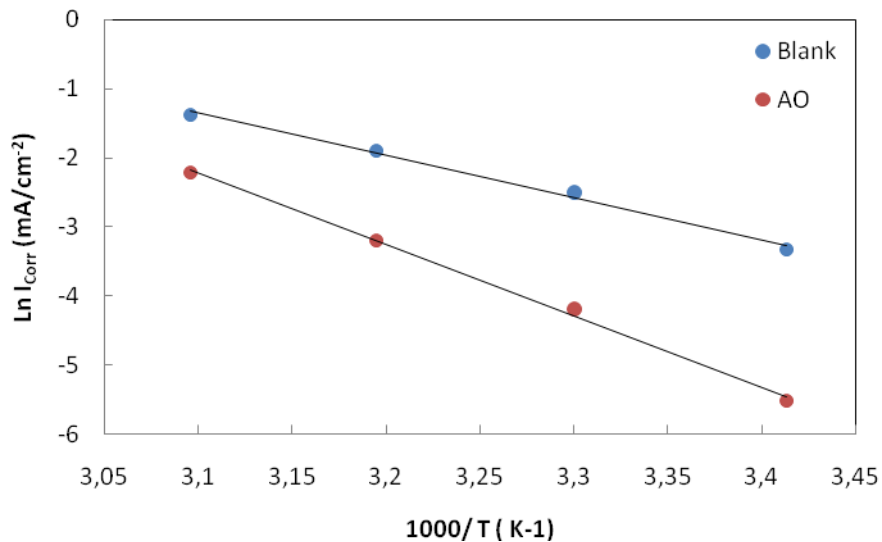


Figure 7. Arrhenius plots of copper in (2M H₃PO₄ + 0.3 M NaCl) with and without 6 g/L of AO.

The activation energy values obtained are 50 and 84 kJ/mol for copper corrosion in 2M H₃PO₄ + 0.3 M NaCl in presence and in absence of AO at 6g/L respectively.

It's observed that E_a increases slightly in the presence of AO that indicates the good performance of this inhibitor at higher temperatures. Generally, the inhibitive additives cause a rise in activation energy value when compared to the blank and this could be often interpreted as an indication for the formation of an adsorptive film by a physical (electrostatic) mechanism [44,45].

Kinetic parameters, such as enthalpy and entropy of corrosion process, may be evaluated from the effect of temperature. An alternative formulation of Arrhenius equation is (9) [46]:

$$I_{corr} = \frac{RT}{Nh} \cdot \exp\left(\frac{\Delta S^*}{R}\right) \cdot \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (9)$$

Where N is the Avogadro's number, h the Plank's constant, R is the perfect gas constant, ΔS* and ΔH*the entropy and enthalpy of activation, respectively.

Fig.8 shows a plot of ln(W/T) against 1/T for AO. Straight lines are obtained with a slope of (-ΔH*/R) and an intercept of (ln R/Nh + ΔS*/R) from which the values of ΔH*and ΔS* are calculated respectively (Table 10).

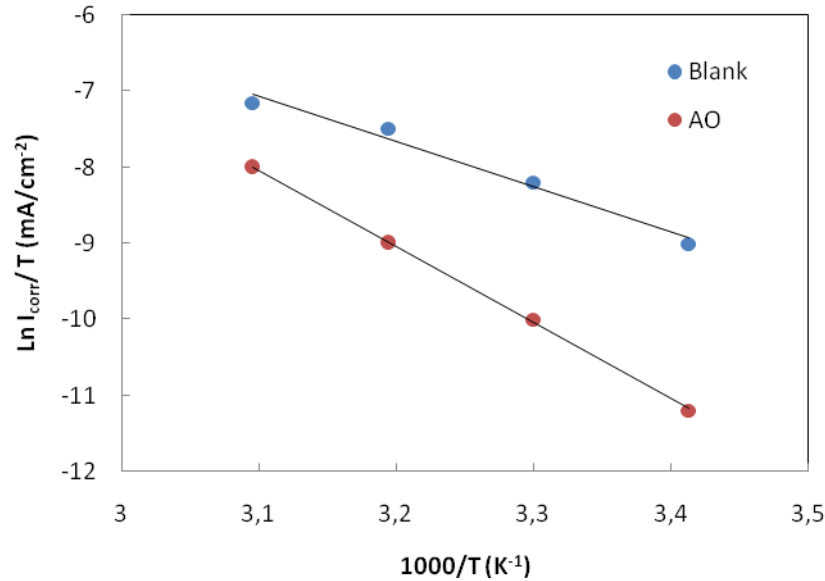


Fig.8 Relation between $\ln(I_{\text{corr}}/T)$ and $1000/T$ at different temperatures.

The value of free energy ΔG^* is deduced from the formula (10):

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (10)$$

Table10. The values of activation parameters ΔH^* , ΔS^* and ΔG^* for copper in (2M H_3PO_4 + 0.3 M NaCl) in the absence and the presence of 6 g/L of AO respectively.

Inhibitors	ΔH^* (kJ/mole)	ΔS^* (J/mole ⁻¹ .k ⁻¹)	ΔG^* (kJ/mole à T=293K)
Blank	48	-111	80
Artimisia oil (6g/L)	83	-011	86

From the data obtained in Table 10, it can be concluded that:

* The signs of the enthalpies ΔH^* reflect the endothermic nature of the copper dissolution process.

* The negative values of ΔS^* pointed to a greater order produced during the process of activation. This can be achieved by the formation of an activated complex representing an association or fixation with consequent loss in the degrees of freedom of the system during the process [47].

The ΔG^ values for inhibited systems were more positive than that for the uninhibited systems revealing that in presence of inhibitor addition the activated corrosion complex becomes less stable as compared to its absence.

4. CONCLUSION

From the overall experimental results, the following conclusions can be deduced:

- The corrosion rate of copper in 2M phosphoric acid depends of chloride concentration. The maximum value is obtained for a chloride concentration equal to 0.3M.
- Artimisia oil (AO) acts as a good inhibitor for the corrosion of copper in 2M H_3PO_4 + 0.3 NaCl.
- The inhibition efficiency of AO increases with the concentration to attain a maximum value 89 % at 6g/L.
- AO is a mixed inhibitor and its molecules block both the anodic and cathodic sites of the metal surface.
- The effect of temperature on the corrosion behavior of copper indicates that inhibition efficiency of the natural substance decreases slightly with the rise of temperature.
- The results obtained from weight loss, polarization and EIS are in reasonably good agreement.

REFERENCES

- [1]. M.A. Hajji, Ph D Thesis, Mohamed V University, Rabat, Morocco (1996).
- [2]. E.M. Jallouli, Second European Colloquium Chemical Plants, Grenoble (1994) p.9.1.
- [3]. A.Bellaouchou, A.Guenbour, A.BenBachir, Corros. Nace 49 (1993)656.
- [4]. S.El.Hajjaji, J.Roy, L.Aries, F.Dabosi, Br.Corros. J. 28(1993)201.
- [5]. N.Bui, A.Irzo, F.Dabosi, A.Guenbour, A.BenBachir, Ann.Chim. 8 (1983) 411.
- [6]. H.Idrissi, J.Mater. Sci. 31(1996)499.
- [7]. M.A.Hajji, A.Guenbour, E.M.Jallouli, A.BenBachir, S.Belcadi, Ann.Chim.Sci.Mater. 274(2002)27.
- [8]. A.Guenbour, J.Faucheu, A.BenBachir, F.Dabosi, N.Bui, Br.Corros. J. 23(1988)234.
- [9]. F.E.White, G.K.Grossmann, H.Decking, Corrosion 52(1996)433.
- [10]. S.O.Benhardson, R.O.Sterholm, Inform. Chim. 176(1978)125.
- [11]. J.Charles, D.Catelin, F.Dupoiron, Mater.Technol. 8(1987)309.
- [12]. A.J. Sedrik, Corrosion 42(1986)376.
- [13]. N. Nassif, Surf.Technol. 26(1985)189.
- [14]. Gokhan Gece, Corrosion Science 53 (2011) 3873.
- [15]. L. Afia, R. Salghi, L. Bammou, Lh. Bazzi, B. Hammouti, L. Bazzi. Acta Metall. Sin. 25(2012) 10-18.
- [16]. A.Y.El-Etre, M.Abdallah, Z.E.El-Tantawy, Corrosion Science 47 (2), (2005) pp. 385-395.
- [17]. E.E. Oguzie, Portugaliae Electrochimica Acta 26(2008)303.
- [18]. E.E. Oguzie, K.L. Iyeh, , A.I. Onuchukwu, Bulletin of Electrochemistry 22(2006)63.
- [19]. E.A. Noor, Journal of Engineering and Applied Sciences 3(2008)23.
- [20]. P.C. Okafor, I.E. Uwah, , E.E. Ebenso, , U.J. Ekpe, S.A. Umoren, Corrosion Science, 50(2008)2310.
- [21]. M. Gong, F.Y. Mao, J.P. Wu, X.-G. Zeng, Corrosion and Protection 27(2006)576.
- [22]. A. Bouyanzer, L. Majidi, B. Hammouti, Bulletin of Electrochemistry 22(2006)321
- [23]. E. E. Oguzie, Corrosion Science 50 (2008) 2993.
- [24]. P. Bothi Raja, M.G. Sethuraman, Materials Letters 62(2008)2977.
- [25]. L. Afia, R.Salghi, El. Bazzi, L. Bazzi, M. Errami, O. Jbara, S. S. Al-Deyab and B. Hammouti, Int. J. Electrochem. Sci., 6 (2011) 5918 - 5939
- [26]. L. Bammou, M. Mihit, R. Salghi, A. Bouyanzer, S.S. Al-Deyab, L. Bazzi and B. Hammouti, Int. J. Electrochem. Sci., 6 (2011) 1454 – 1467.
- [27]. L.Bammou, B.Chebli, R.Salghi, L.Bazzi, B.Hammouti, M.Mihit and H.El Idrissi. Green Chemistry Letters and Reviews 3(2010)173.
- [28]. D. Ben Hmamou, R. Salghi, Lh. Bazzi , B. Hammouti, S.S. Al-Deyab, L. Bammou, L. Bazzi, A. Bouyanzer. Int. J. Electrochem. Sci. 7(2012)1303.
- [29]. Anonymous. French Pharmacopoeia. Maison neuve SA: Moulins-les-Metz. France. 1983.
- [30]. E. Stenhagen, S. Abrahamsson, F.W. McLafferty. Registry of Mass Spectral Data. John Wiley: New York. NY. 1974.
- [31]. R.P. Adams, Allured: Carol Stream. IL. 1995.
- [32]. M. mihit, S. El issami, M. Bouklah, L. Bazzi, B. Hammouti, E. Ait Addi, R. Salghi, S. Kertit, Applied Surface Science 252(2006)2389.
- [33]. K.F. Khaled, Sahar A. Fadl-Allah, B. Hammouti, Materials Chemistry and Physics 117 (2009)148.
- [34]. M. Mihit, Ph D Thesis, Ibn Zohr University, Agadir, Morocco (2006)
- [35]. Orlin Blajiev, Annick Hubin, Electrochimica Acta 49 (2004) 2761.
- [36]. E.M. Sherif, S.M. Park, J. Electrochem. Soc. 152(2005)428.
- [37]. C.W. Yan, H.C. Lin, C.N. Cao, Electrochim. Acta 45(2000)2815.
- [38]. A. ElWarraky, H.A. El Shayeb, E.M. Sherif, Anti-Corros. Methods Mater., 51(2004)52.
- [39]. M. Bouklah, B. Hammouti, M. Lagrenee, F. Bentiss Corrosion Science 48 (2006) 2831.
- [40]. T. Tsuru, S. Haruyama, B. Gijutsu, J. Jpn. Soc. Corros. Eng. 27(1978)573.
- [41]. H. Shih, H. Mansfeld, Corrosion Science 29(1989)1235.
- [42]. S.Martinez, M.Metikos-Hukovic, J.Appl. Electrochem. 33(2003)1137.
- [43]. M. Bouklah, A. Attayibat, S. Kertit, A. Ramdani, B. Hammouti, Appl.Surf. Sci. 242(2005)399.
- [44]. A. Popova, E. Sokolova, S. Raicheva, M. Christov, Corrosion Science 45 (2003) 33.
- [45]. T. Szauer, A. Brandt, Electrochim. Acta 22 (1981) 1209.
- [46]. S.S. Abd-El-Rehim, S.A.M. Refaey, F.Taha, M.B.Saleh, R.A.Ahmed, J.Appl. Electrochem. 31(2001)429.