



Research Article

Inhibition of copper corrosion by the essential oil of *Allium sativum* in 0.5M H₂SO₄ solutions

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Abstract

Materials in general and copper in particular, have a wide variety of industrial applications. However, they can easily corrode in aggressive environments. The anticorrosive action of copper by the essential oil of *Allium sativum* in a 0.5M H₂SO₄ solutions has been studied using electrochemical techniques: electrochemical impedance spectroscopy and potentiodynamic polarization. The polarization curves indicate that the studied oil acts as a cathodic inhibitor retarding the cathodic reaction. An appropriate electrical equivalent circuit model was used to calculate the electrochemical impedance parameters. The results obtained showed that the inhibition efficiency depends on the inhibitor concentration and the temperature. This efficiency reached 97% at a concentration of 1.0 g/L. Some thermodynamic parameters for activation process and metal dissolution such as activation energy (E_a) activation entropy (ΔS_a) and the activation enthalpy (ΔH_a) were also calculated and discussed.

Keywords Corrosion · Inhibition · Copper · Garlic · Adsorption · Sulphuric acid

1 Introduction

Due to its excellent thermal conductivity, electrical conductivity, ductility, and good workability, copper is widely used in various fields, such as machinery manufacturing, power transmission, cooling and heating systems, military industry, and so on [1–4]. In order to obtain a shiny final copper surface, which is required in some applications, or to remove scale deposits that reduce the heating efficiency of some copper-based equipment, a sulphuric acid solution is frequently used to remove any undesirable products formed at the surface (oxidation films, incrustations, scale etc.) [3–5]. Therefore, corrosion of copper can be caused during this chemical treatment after the scale or oxides have been removed, which implies the dissolution of the metal and the consumption of the acid used. This also implies important economic losses for

the industrialists [6, 7]. Corrosion phenomenon can be reduced by the use of inhibitors.

According to the literature, several studies have been carried out in this field for hundreds of years [8–10]. In 1860 Great Britain announced the discovery of the world's first corrosion inhibitor. Since this discovery, a lot of work has been done to find and develop different types of organic and inorganic inhibitors [11]. Previous studies have found that the presence of heteroatom's such as nitrogen, sulphur and phosphorus in the molecular structure of these inhibitors improves their inhibition effectiveness. Therefore, they can establish a coordination bonds between the free doublets of these heteroatom's and the empty d-orbital's of transition metals, which indicate the formation of an effective barrier film that isolates the metal substrate from the corrosive environment [12, 13]. However, some of these inhibitors

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have disadvantages: high cost, toxic to humans, risk of pollution to the environment [14]. In this context, corrosionists have always sought alternatives by focusing on biodegradable, economical, renewable plant products that do not present any risk to human health and the environment [15, 16].

According to Ajeigbe et al. [17] and Barakat et al. [18], plant extracts have been used for decades as effective corrosion inhibitors, their property due to their richness in complex organic compounds containing heteroatom's, aromatic rings and multiple bonds (double and triple bonds) have also been identified as adsorption centers that interact with active sites on the surface of a metal. For this reason, multiple essential oils from different plants have also been studied to prevent metal corrosion. Among these plants, *Rosmarinus officinalis* L [19], *Nigella Sativa* [20], *Artemisia herba-alba's* [21], *Juniperusphoenicea* [22] and *Cinnamon* [3]. All these oils have shown good inhibitory properties.

Garlic or *Allium sativum*, which belongs to the Liliaceae family has been widely used since antiquity due to its therapeutic properties in the field of pharmacology [23, 24].

It has been evaluated as effective corrosion inhibitors in various media by several investigators. Table 1 shows some of the work of *A. sativum* used as corrosion inhibitors of different materials in different environments.

The essential oil of *A. sativum* is characterized by a high amount of organo-sulphur compounds such as trisulfide, methyl-2-propenyl; trisulfide, di-2-propenyl and diallyl disulfide [30]. The last compound has been tested as a corrosion inhibitor of copper corrosion in 0.5M sulfuric acid medium by Tan et al. [4]. The existence of these products in our essential oil means that it may be an excellent inhibitor candidate for reducing copper corrosion in acidic media. Therefore, the aim of this work is to study the inhibition of copper corrosion in 0.5M sulphuric acid media in the absence and presence of *A. sativum* essential oil using electrochemical techniques such as potentiodynamic study, electrochemical impedance spectroscopy (EIS) and surface analysis by SEM/EDX.

Table 1 List of *A. sativum* used as corrosion inhibitors

Nature of inhibitor	Metal	Electrolyte	Ref
Garlicextract	Aluminum	0.5M HCl	[25]
Peel garlicextract	Carbon steel	0.5M HCl	[26]
Garlicextract	Mild steel	HCl% 5–20 5–20% mud acid	[27]
Garlicextract	Mild steel	3%NaCl	[28]
Garlic essential oil	Carbon steel	1 M HCl	[29]

2 Materials and methods

2.1 Extraction of the essential oil of *A. sativum*

The essential oil of garlic was extracted by hydrodistillation in a simple distillation unit, from fresh garlic bulbs of *A. sativum* (Meknes region, Morocco), prepared and distilled according to the following method: 500 g of garlic cloves were mixed with 500 ml of distilled water in a domestic blender for 1 min, and then placed in a 1L flask. The distillation was carried out for 4 h. The distillate (hydrolyat + essential oil) was collected in a flask and separated with a separating funnel using diethyl ether as solvent. The organic phase, containing the essential oil, obtained was passed through a rotavapor to get rid of the solvent. The product obtained is kept in a dark brown glass container and stored in a refrigerator at 2 to 5 °C.

2.2 Preparation of the material

The metal samples used in this study are copper samples with the following chemical composition (in % by weight): 0.019 P, <0.001 Fe, <0.001 As, <0.001 Mn, <0.002 Sb, <0.001 Al, 0.009 Sn, 0.003 Ni, 0.015 Pb, <0.005 Ag, <0.001 Bi, <0.001 S, <0.005 C and the rest is Cu. The copper samples were abraded with different grades of SiC abrasive papers (from 180 to 2000), followed by cleaned carefully according to ASTM G-81, and finally drying at room temperature. The aggressive solution were prepared by diluting analytical grade H₂SO₄ (98 wt.%) with distilled water. The concentration of the *A. sativum* oil used in the present study ranged from 0.5 to 2.0 g/L, and the blank solution was also prepared for comparison.

2.3 GC–MS analysis

The chromatographic analysis of the studied essential oil was carried out at the University Centre for Analysis, Expertise, Technology Transfer and Incubator CUA2TI of IBN TOFAIL University in Kenitra, using a 456-GC type gas chromatograph coupled to an EVOQ TQ type mass spectrometer. The fragmentation is performed by electronic impact at 70 eV. The column used is a Rxi-5Sil MS type capillary column (30 m × 0.25 mm ID × 0.25 μm df). The temperature of the column is initially programmed at 40 °C for 8 min at a rate of 2 °C/min up to 200 °C or 20 min remaining. The carrier gas is helium with a flow rate of 1.50 ml/min. The injection temperature is maintained at 250 °C and the injection volume is 1 μl. The apparatus is connected to a computer system managing a NIST MS Search2.0 mass spectrum library and driven by Ms Data review software

allowing to follow the evolution of the chromatographic analyses. The identification of the constituents has been made on the basis of the comparison of their retention times with those of the standard compounds in the computerized database (NIST 2014).

2.4 Electrochemical measurements

The electrochemical measurements were carried out using a potentiostat/galvanostat/PGZ100 controlled by Volta Master 4 analysis software. The electrochemical experiments were carried out in the assembly of a three-electrode electrochemical cell which the size is 50 ml, using a copper plate as working electrode (with an exposed surface area of 1 cm²), a platinum rod as counter electrode and saturated calomel electrode (SCE) as reference electrode.

EIS measurement was performed in the frequency range of 100 kHz to 10 MHz at an open circuit potential (OCP) with 10 points per decade. The applied AC signal amplitude is 10 mV ms. All experiments were performed after 30 min immersion of the copper in a 0.5M H₂SO₄ solutions in the absence and presence of different concentrations of the studied oil.

The potentiodynamic polarization curves were obtained by sweeping the working electrode potential from – 1200 to 600 mV with a sweep rate of 1 mV/s. All electrochemical experiments were carried out at a temperature of 298 K and were repeated three times and presented values were obtained by averaging.

2.5 Analysis of surface morphology

In order to confirm the formation of a natural film on the cooper surface exposed to the 0.5M H₂SO₄ solutions for 6 h in the absence and presence of the *A. sativum* oil was carried out by analysis using Scanning Electron Microscope (Quantra 450) coupled with EDX analyses. These analyses were carried out at the MASCI Foundation—Rabat.

3 Results and discussion

3.1 Analysis by GC–MS

GC–MS analysis identified 16 compounds representing 99.815% of the total constituents listed in Table 2.

Allium sativum essential oil from the region of Meknes is composed essentially of organosulphurates and hydrocarbons, comparing these results with the literature [31–33], it was noticed that there is a great variation in the level of the elements identified, as well as in their percentages of existence in the oil studied, this variation may be due to the

Table 2 Composition of the essential oil of *A. sativum* Moroccan from the Meknes region

TR	Chemical compound	Percentage of existence (%)
5,998	Disulfide, methyl2-propenyl	3.669
6,996	(E)—methyl-2-(prop-1-en-1-yl)disulfane	0.511
7,928	3H-1,2-dithiole	0.121
8,257	Trisulfide, dimethyl	1.488
14,085	Diallyldisulphide	26.623
15,136	(E) 1-Allyl-2-(prop-1-en-1-yl)disulfane	2.359
15,495	(Z) 1-Allyl-2-(prop-1-en-1-yl)disulfane	5.171
17,661	Trisulfide, methyl2-propenyl	16.459
28,064	Trisulfide, di-2-propenyl	34.104
33,111	1-3 Dithiane	1.111
42,485	2-Vinyl-1,3-dithiane	2.794
63,662	Hexadecen-1-ol,trans-9	1.011
77,934	1-Docosene	1.686
91,395	Hexacosane	0.75
98,434	Dotriacontane	0.47
104,749	Pentatriacontane	1.488

Bolditalic indicate the major compounds

origin of the plant [34] as it may be due to the operating conditions of extraction [35].

Satyral [36] was able to identify 33 organosulfur compounds for Spanish garlic oil, the majority of which are Diallyltrisulfide (33.4%), Allyl methyl trisulfide (19.2%), and Diallyl disulfide with a percentage of (20.8%), whereas Egyptian garlic oil had diallyl disulfide (25.2%), allyl methyl trisulfide (23.8%), and diallyltrisulfide (21.1%) as major constituents [33]. The major constituents in this study are: Diallyl disulfide (26.623%), Trisulfide, methyl2-propenyl (16.459%) and Trisulfide, di-2-propenyl (34.104%) shown in Table 3.

3.2 Polarization curve

The polarization curves of copper in the 0.5M H₂SO₄ solutions in the absence and presence of the essential oil of *A. sativum* at 298 K are shown in Fig. 1:

In the literature the behavior of copper in an aerated sulphuric acid solution has been studied by several researchers [37–40], the cathodic reaction was the summation of Eqs. (1) and (2):

Hydrogen reduction (1):



Reduction of oxygen (2):



Table 3 Main constituents of *A. sativum* essential oil

Chemical compound	Diallyldisulphide	Trisulfide, methyl2-propenyl	Trisulfide, di-2-propenyl
Structure	<chem>C=CCSCC=C</chem>	<chem>CSCCSCC=C</chem>	<chem>C=CCSCC=C</chem>
Percentage (%)	26.623	16.459	34.104
Molecular weight (g/mol)	146.27	152.30	178.34

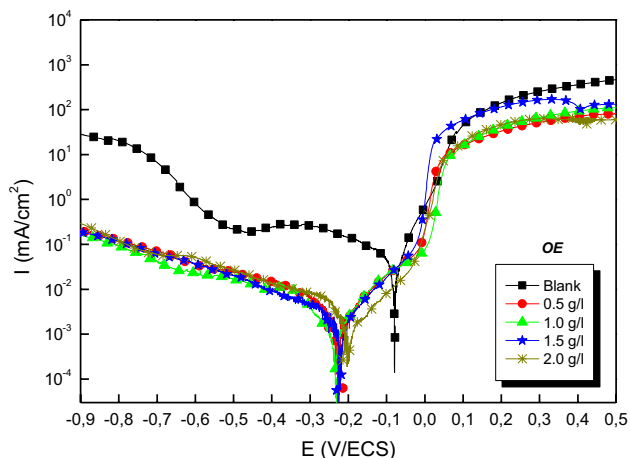


Fig. 1 Polarization curves of copper in 0.5M H₂SO₄ solutions in the presence and absence of *A. sativum* essential oil (OE)

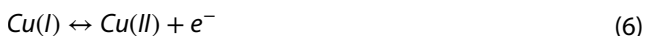
The cathodic reduction of oxygen can be expressed either by a direct transfer of 4e⁻ as described by Eq. (2) or by 2e⁻ in two consecutive steps involving reduction with hydrogen peroxide (H₂O₂) first [41, 42]:



followed by a further reduction:



The anodic dissolution of copper takes place in two continuous stages.



It has been concluded that the reaction rate of the first stage (reaction 5) is much faster than that of the second stage (reaction 6); therefore, the second stage is considered to be a key stage in the corrosion process [43].

The anodic and cathodic polarization curves shown in Fig. 1 show that the corrosion potential has been shifted to more negative values by increasing the concentration of the inhibitor.

On the other hand, the cathodic current density has been remarkably reduced compared to the anodic current density, implying that the rate of cathodic corrosion has been reduced. Also, it can be observed that the cathodic curves are not parallel to the white curve, which states that the inhibitor causes the modification of the cathodic corrosion mechanism of copper in an aerated 0.5M H₂SO₄ solutions by influencing the cathodic oxygen reduction reaction more than the anodic copper dissolution reaction [14].

The electrochemical parameters obtained from the extrapolation of the Tafel lines are listed in Table 4. These parameters included the corrosion potential (E_{corr}), the cathodic Tafel slope(β_c) and the corrosion current density (i_{corr}). In addition, the corrosion inhibition efficiency (η_{pp}) was obtained using the following formula [43]:

$$\eta_{pp} \% = \left[\frac{(i_{corr}^{\circ} - i_{corr})}{i_{corr}^{\circ}} \right] \times 100$$

where i_{corr}[°] and i_{corr} are the corrosion current densities values in absence and presence of inhibitor, respectively.

The parameters presented in Table 4 show that all corrosion potentials are transferred to more negative potentials with a degree of offset of - 150 mV exceeding a value of - 85 mV. This observation reveals that the studied compound is cathodic in nature [4, 13, 44].

Moreover, the i_{corr} values decrease towards lower current densities than the uninhibited solution with

Table 4 Electrochemical parameters of the potentiodynamic curves for copper at 298 K in 0.5M H₂SO₄ solutions with and without different inhibitors concentrations

Inh	Conc (g/L)	E _{corr} (mV/ECS)	i _{corr} (μA/cm ²)	-β _c (mV/dec)	η _{pp} (%)	R _p (Ω cm ²)	η _{RP} (%)
Blank	-	-79	29.0	204	-	397	-
OE	0.5	-213	1.2	188	95.8	8936	95.5
	1.0	-229	0.7	165	97.6	15,182	97.4
	1.5	-217	0.8	170	97.2	13,000	96.9
	2.0	-196	1.4	154	95.1	7343	94.6

increasing concentration, which means the increase of the inhibition efficiency up to a value of 97.6% at a concentration 1 g/L. This phenomenon proves the formation of a barrier film on the surface of copper against corrosive attack [45].

The polarization resistance (R_p) values of copper in 0.5M H_2SO_4 increases from 397 Ω for the blank to 15182 Ω for 1.0 g/L concentration of *A. sativum* (Table 4).

3.3 Electrochemical impedance spectroscopy

1 In order to obtain information on the protection mechanism (charge transfer, diffusion, and adsorption) of copper by *A. sativum* essential oil in 0.5M H_2SO_4 solutions, electrochemical impedance measurements has been performed. Many works [46, 47], have shown that the electrochemical impedance measurements are likely to reveal the elementary steps involved in the global corrosion and/or protection processes. Cruz et al. [48] and Bentiss et al. [49] have studied the inhibition mechanism of some inhibitors using electrochemical impedance measurements, seems to prove that this technique is particularly well adapted to the

determination of the mode of action of the inhibitors, to the evaluation of the dielectric characteristics of the formed film and makes it possible to follow their evolution according to many parameters.

The Nyquist diagrams of copper immersed in the 0.5M H_2SO_4 solutions obtained experimentally without and with the addition of different concentrations of *A. sativum* essential oil studied are recorded in Fig. 2. The observed experiments tested of triplicate measurements are highly reproducible giving standard deviations.

The impedance diagrams presented in the Nyquist plane are characterized by the presence of two badly separated capacitive loops, we can confirmed this result by the bode diagram, a two time-constants in bode plot appears in the inhibited sample as shown in Fig. 2b. The semicircle at the high frequency part is related to the resistance and capacitance of adsorbed inhibitor films present on the copper surface, the second time constant appearing at low frequencies corresponds to the charge transfer phenomenon at the copper/ H_2SO_4 interface [3].

From the bode presentation, concerning the bode presentation of blank solution (Fig. 2a) we can observed

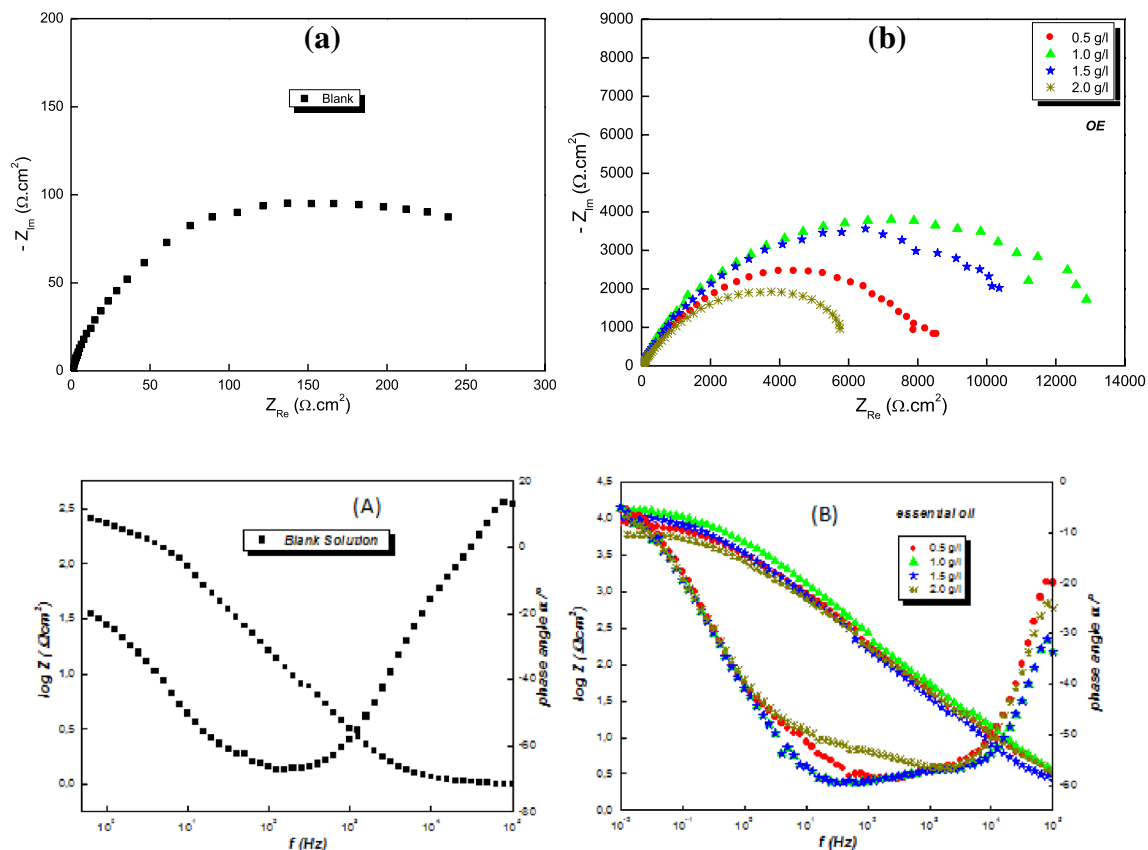


Fig. 2 Nyquist and Bode diagrams copper/0.5M H_2SO_4 interface in the Nyquist plane in the absence (a) and presence of *A. sativum* (b) at different concentrations at 298 K

the presence of one time-constant attributed to charge transfer process.

We also observe that the impedance display of copper in the solutions containing the inhibitor has considerably changed shape and size compared to the blank one. While the essential oil of *A. sativum* leads to changes in impedance behavior [3], the increase in the size (namely R_p = diameter) of these loops, with the concentration of inhibitor is justified, indicating an increase in the protective power by the formation of an inhibitor film that blocks the formation of the corrosion product [50]. This result reflects the influence of *A. sativum* on the process at the copper/acidic medium interface [51].

The Nyquist impedance spectra of copper in 0.5M H_2SO_4 were modelled by the equivalent circuit shown in Fig. 3a, and All impedance spectra obtained from the copper electrode exposed for 30 min in H_2SO_4 solutions containing *A. sativum* were analyzed by the equivalent circuit shown in Fig. 3b. The following are the components of the suggested equivalent circuit: R_s represents the solution resistance, R_{ct} the charge transfer resistance, R_f the film resistance, and Q_f and Q_{dl} the constant phase elements [51, 52].

As can be seen in Fig. 3, the capacitor has been replaced by a constant phase element, indicating the presence of a dissimilar frequency response. The EPC impedance is defined as follows [53]:

$$Z_{CPE}(\omega) = Q^{-1}(j\omega)^{-n}$$

where Q is a constant in $\Omega/cm^2 s^n$, ω is the angular frequency in rad/s, n is the exponent of CPE with $-1 < n < 1$.

CPE can represent an inductance ($n = -1$), a Warburg impedance ($n = 0.5$), a pure capacitance ($n = 1$), or a resistance ($n = 0$). The smaller value of n , the higher the surface roughness [54].

The electrochemical parameters obtained from the impedance diagrams and the inhibiting efficiency ($E\%$) are grouped in Table 4. The values of the polarization resistance R_p of all systems are calculated using the following equation:

$$R_p = R_f + R_{tc}$$

Inhibition efficiency ($\eta_{imp\%}$) is calculated by the following equation [45]:

$$\eta_{imp\%} = (R_p - R_p^{\circ})/R_p \times 100$$

where R_p° and R_p are the charge transfer resistance in absence and presence of the inhibitor, respectively.

From the data in Table 5, it can be seen that, when the concentrations of *A. sativum* increase to a value of 1 g/L, the values of R_{ct} increase, while the values of Q_{dl} decrease, this is due to the formation of a protective film on the metal surface by the adsorption of *Allium sativum*, which slows down the corrosion process of copper in H_2SO_4 by the action of the inhibitor [50]. The decrease in Q_{dl} value may be due to a decrease in the local dielectric constant and/or an increase in the thickness of the double layer [50]. As a consequence, it can be said that the inhibitor molecules act by adsorption at the solution-metal interface [51].

Similarly, when the concentration of the inhibitor increases to a value of 1 g/L, it can be seen that the R_f

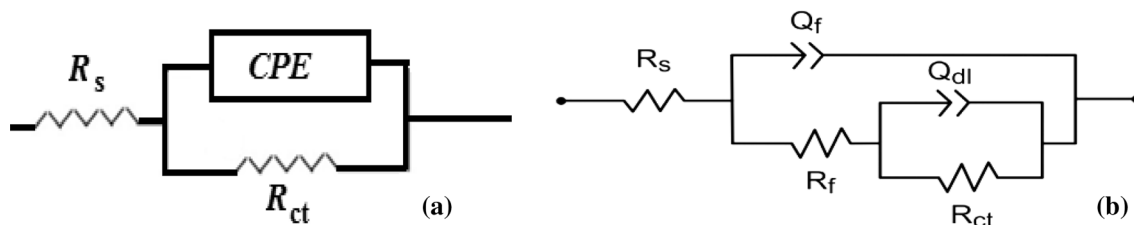


Fig. 3 Equivalent circuits for the copper EIS used to model the copper/solution interface in the absence (a) and in the presence of the inhibitor (b)

Table 5 Electrochemical impedance parameters in the absence and presence of *A. sativum* at different concentrations at 298 K

Inhibitor	Conc (g/L)	R_s (Ωcm^2)	Q_f ($\mu F cm^2$)	n_f	R_f (Ωcm^2)	Q_{dl} ($\mu F cm^2$)	n_{ct}	R_{ct} (Ωcm^2)	R_p (Ωcm^2)	$E\%$
Blank	–	0.7 ± 0.1	–	–	–	475 ± 1.5	0.72 ± 0.01	350 ± 1.5	350	–
<i>Allium sativum</i>	0.5	2.6 ± 0.2	57.7 ± 1.2	0.688 ± 0.004	5657 ± 2.3	120 ± 0.8	0.843 ± 0.02	2809 ± 1.2	8466	95.8
	1.0	2.2 ± 0.4	46.1 ± 1.5	0.683 ± 0.005	6173 ± 2.5	41 ± 0.4	0.795 ± 0.01	8129 ± 2.0	14,302	97.5
	1.5	2.2 ± 0.3	66.0 ± 1.3	0.700 ± 0.003	5639 ± 3.0	52 ± 0.6	0.493 ± 0.008	6519 ± 1.8	12,158	97.1
	2.0	2.1 ± 0.1	77.6 ± 2.0	0.655 ± 0.004	4479 ± 2.8	162 ± 0.2	0.718 ± 0.009	2342 ± 1.3	6821	94.8

values increase, while the Q_f values decrease to the optimal concentration (1 g/L of *A. sativum* essential oil). These evolutions indicate a thickening of the film formed and a decrease in permeability through it [55]. Consequently, the decrease in Q_f values shows that the adsorption layer formed by *Allium sativum* on the metal surface is stable and thick [56]. In the presence of 1.0 g/L of *Allium sativum* we notice that the diameter of R_p has obviously increased from $350 \Omega \text{ cm}^2$ to $14,302 \Omega \text{ cm}^2$, which implies a better protection of the copper by our oil in an acidic environment.

Comparing the performance of our oil to other green inhibitors such as cinnamon essential oil and lotus zizyphus extract which have been tested for the same metal in an acidic medium we notice that the maximum efficiency that can be achieved with cinnamon essential oil is 89.62% [3] as well as obtaining a maximum value of 90.57% for the extract of lotus zizyphus [50], while with the oil of *A. sativum* the effectiveness has reached 97.5% Table 5, so we can see that our inhibitor admits a better inhibitory effect for copper in an acidic medium compared to these two green inhibitors.

3.4 Temperature effect

In order to evaluate the influence of temperature on the inhibition efficiency of the investigated essential oil, the polarization curves of copper were performed before and after addition of *A. sativum* in 0.5M H_2SO_4 solutions at a concentration of 1.0 g/L in the temperature range from 298 to 328 K after 30 min of immersion time.

Figure 4 shows the polarization curves of copper in the 0.5M H_2SO_4 solutions in the absence (a) and presence (b) of the inhibitor. The electrochemical parameters are

summarized in Table 5. It can be seen from Table 5 that the cathodic and anodic current densities increase with increasing temperature. Thus, this compound still show superior inhibition performance to prevent copper from corrosion by forming a firm adsorption film onto copper substrate.

On the other hand, it can be seen that the curves in Fig. 4a are more or less parallel to each other, only for the anode region, whereas the cathode region admits a change in the shape of the cathode curve from $T=298 \text{ K}$ to $T=308 \text{ K}$, which implies that temperature does not affect the anode reaction but only the cathode reaction and the speed of the latter.

Although in the presence of the inhibitor Fig. 4b, it can be seen that the curves are more or less parallel for the two cathodic and anodic regions, it can be said then that in the presence of the inhibitor the temperature does not affect the mechanism but only the corrosion rate.

Compared with that in blank solution, the i_{corr} value decreases remarkably with the addition of 1.0 g/L d'E.O. at each temperature, implying that this essential oil considerably inhibit the corrosion reaction of MS.

Also by comparing the curves of Fig. 4 we can see a decrease in the current density i_{corr} compared to the bank solution at different temperatures as well as a decrease in the inhibition efficiency with temperature which can be due to the weakening of the adsorbed film on the substrate surface, which suggests a physical adsorption of our inhibitor on the metal surface [57].

The effect of temperature on the inhibited acid-metal action is very complex, many changes may occur on the metal surface, such as rapid desorption of the inhibitor as well as the inhibitor itself, may undergo decomposition, rearrangement or both at the same time [3, 50].

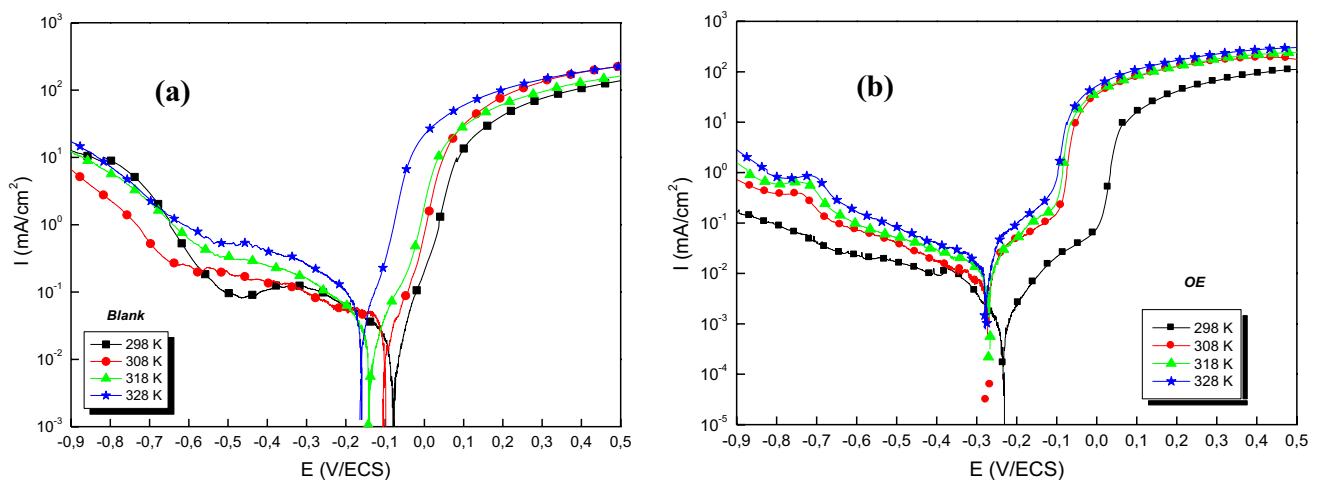


Fig. 4 Potentiodynamic polarization curves for copper in 0.5M H_2SO_4 without (a) and with 1.0 g/L of *A. sativum* essential oil (OE) (b) at different temperatures

Table 6 Electrochemical parameters of copper in 0.5M H₂SO₄ solutions with and without 1 g/L E.H. of *A. sativum* at different temperatures

Compound	Temperature (K)	-E _{corr} (mV/ECS)	i _{corr} (μA/cm ²)	-β _c (mV/dec)	E (%)
Blank	298	79	29.0	204	-
	308	105	35.0	188	-
	318	142	56.0	164	-
	328	166	77.0	152	-
1.0 g/L d'E.O	298	229	0.7	165	97.6
	308	264	1.8	175	94.8
	318	267	4.5	158	91.9
	328	270	8.8	144	88.5

Table 7 Activation parameters E_a, ΔH_a and ΔS_a for copper in 0.5M H₂SO₄ solutions with and without 1 g/L of *A. sativum* essential oil

Compound	E _a (kJ/mol)	ΔH _a (kJ/mol)	ΔS _a (J/mol/K)
Blank	27.5	25.0	-134.0
1.0 g/L E.O	69.2	66.6	-23.9

Further, Table 6 indicates that corrosion efficiency decreases with increasing temperature, this decrease in efficiency is attributed to the increased dissolution of copper in acidic media, and/or partial desorption of the inhibitor from the metal surface [58–60]. These results indicate physisorption of the inhibitor on the metal surface of copper [50, 58].

3.5 Parameters for activation of the corrosion process

The calculation of thermodynamic parameters such as activation energy, activation enthalpy and activation entropy allow the quantification of the corrosion inhibition efficiency in order to determine and interpret the adsorption type adopted by an inhibitor.

In order to estimate these parameters shown in Table 7, plots of the Arrhenius curves, the logarithm of the corrosion rate (ln(i_{corr})) vs (1000/T) are used (Fig. 5a). The activation energy of the corrosion process E_a can be calculated using the following equation [61, 62]:

$$\ln(i_{corr}) = \ln A - \frac{E_a}{RT}$$

where R is the perfect gas constant, A is the pre-exponential Arrhenius constant and T is the absolute temperature.

The activation entropy (ΔS_a) and the activation enthalpy (ΔH_a) were obtained on plotting (Ln(i_{corr}/T)) vs (1000/T) (Fig. 5b), where (-ΔH_a/R) is the slope and [Ln(R/Nh) + (ΔS_a/R)] the intersection of the straight line with the y-axis according to the alternative formula of the Arrhenius equation [61–63]:

$$\ln\left(\frac{i_{corr}}{T}\right) = \left(\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_a}{R}\right) - \frac{\Delta H_a}{RT}$$

where h is the Planck’s constant, N is the Avogadro number, T is the absolute temperature, ΔS_a is the activation entropy and ΔH_a is the activation enthalpy. The obtained results are grouped in Table 7.

The Arrhenius curves obtained in the presence of 1 g/L of *A. sativum* essential oil presented in Fig. 5 are compared to those of copper in a 0.5M H₂SO₄ solutions in the absence of inhibitor.

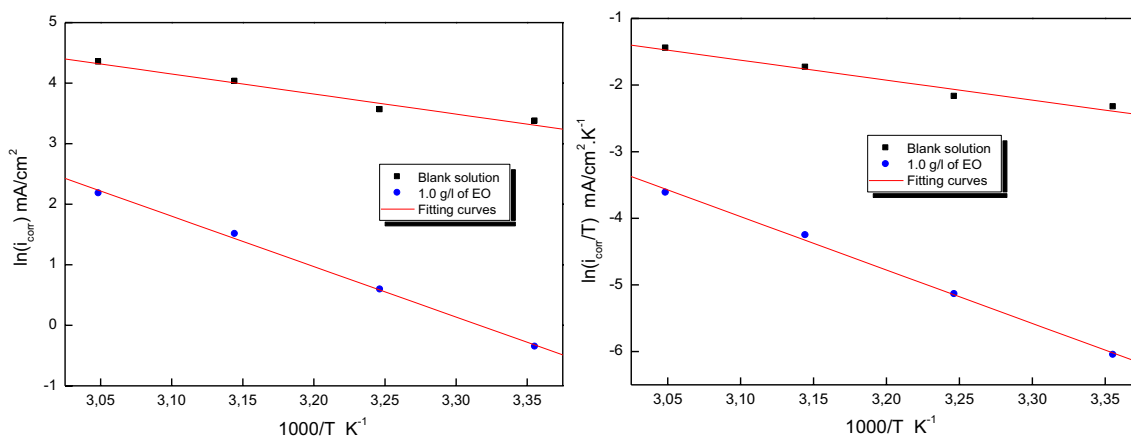


Fig. 5 Arrhenius curves for copper in 0.5M H₂SO₄ solutions with and without 1 g/L of *A. sativum* essential oil

According to the literature, the variation of kinetic parameters adopts a specific type of adsorption. The presence of the studied inhibitor increased the energy barrier (E_a) of the inhibiting solution above that of the blank and hence the inhibition process, which promotes electrostatic interactions with the metal surface and the adsorption of the protective film is of physical nature [3, 63–65]. In contrast to an equivalent chemical adsorption of a decrease in E_a in the presence of an inhibitor, which is accompanied by an increase in the effectiveness of the inhibition with temperature [66, 67].

The results shown in Table 6 indicate an increase in E_a values in the presence of inhibitor compared to the blank solution, which suggests a physisorption at the metal surface, while the studied inhibitor blocks the cathodic sites by constructing a barrier that mainly inhibits the corrosion process [62]. Furthermore, the positive values of ΔH_a indicate the endothermic character of the copper dissolution process and inform that the dissolution of copper is slow in the presence of inhibitor [61, 63]. Also, the negative values of the entropy (ΔS_a) indicate a decrease in the degree of randomness which occurred when the reactants are transformed to activated complexes [61, 63].

3.6 Surface analysis

In order to confirm the results obtained by the electrochemical measurements. Qualitative microscopic SEM analyses coupled with quantitative EDX analyses were performed. Figure 6 shows the surface of recently abraded copper immersed in the 0.5M H_2SO_4 solutions without inhibitor, it can be found that the homogeneous corrosion of the entire copper surface is very dense and orderly in the blank solution. However, the corrosion degree of the Cu surface is very serious. However, the

addition of the studied essential oil causes a decrease in the corrosion degree on the copper surface and a non-uniform protective film is formed on the surface of the copper (Fig. 7).

The EDX analysis (Fig. 6) shows the presence of oxygen, which is a corrosive element for copper and therefore justifies the corrosion of copper. These findings are confirmed by the SEM analysis. Figure 7 shows also the appearance of a sulphur peak which is the initial element of the chemical composition of *A. sativum* essential oil. These observations prove the formation of a protective barrier film created when the tested essential oil interact with the copper surface in acid solution.

3.7 The mechanism of inhibition

Generally, organic molecules presented in our essential oil are adsorbed on the metal surface and prevent further dissolution of metal by blocking either the cathodic or anodic reaction or both. Organic inhibitors, capable of forming insoluble complexes, or chelates, with metallic ions present on the surface of metal [68]. The inhibition efficiency of our corrosion inhibitor (major constituents) against the corrosion of copper in 0.5M H_2SO_4 can be explained on the basis of the number of adsorption sites, their charge density, molecular size, mode of interaction with the metal surface and the ability to form a metallic complex. The π electrons and free electrons on the S atoms form bonds with the metal surface (copper); see Fig. 8.

According to the potential–pH diagram [69], the protective Cu_2O and CuO oxide films can be easily dissolved at low pH values. As shown in Fig. 8, the dissolution of copper in acidic medium proceeded according to the following steps:

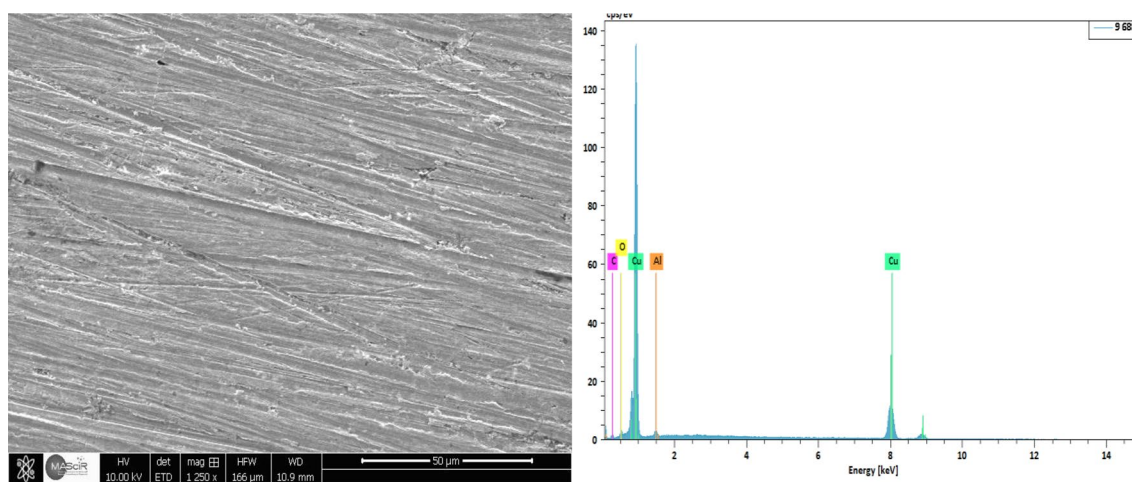


Fig. 6 SEM image and corresponding EDX spectra at the surface of copper immersed for 6 h in 0.5M H_2SO_4 solutions at 298 K

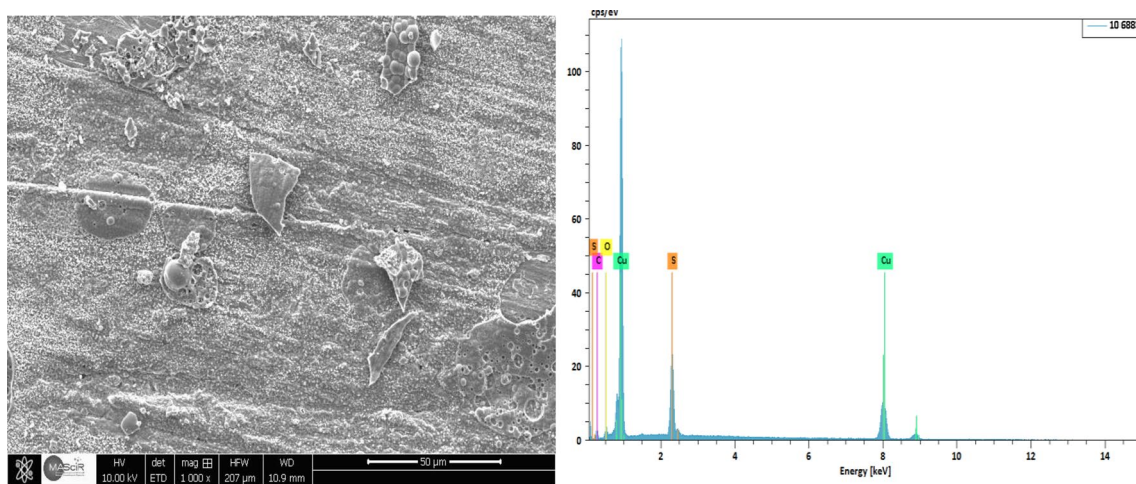
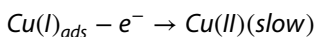
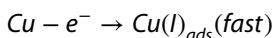
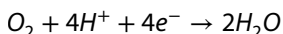


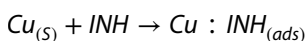
Fig. 7 SEM image and corresponding EDX spectra at the surface of copper immersed for 6 h in 0.5M H₂SO₄ solutions at 298 K with the addition of 1 g/L of the inhibitor



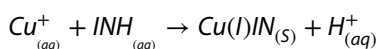
where Cu(I)_{ads} is an adsorbed species at the copper surface and does not diffuse into the bulk solution. The cathode reduction of oxygen can be expressed as follow:



According to the literatures [70] two mechanisms have been proposed to explain the high inhibiting efficiency recorded for the inhibitors designated as INH. One mechanism attributes the phenomenon to the formation of an adsorbed layer of INH i.e.,



where Cu: INH_(ads) refers to INH adsorbed on the copper surface. The other mechanism postulates a protective Cu(I) IN film on the surface, which inhibits the anodic dissolution reaction, i.e.,



The Cu(I)IN complex is favored at more anodic potentials in less acidic media; however, the adsorbed species is formed in more acidic media under cathodic potentials.

4 Conclusion

In the present study, the inhibition effect of *A. sativum* essential oil against the corrosion of copper in 0.5 H₂SO₄ was evaluated via electrochemical and surface studies. From the above results and discussion, we can conclude that:

- The analysis of the oil by GPC-MS showed that the oily fraction of garlic contains highly reactive sulphur molecules of which three are the main compounds (diallyldisulphide, trisulphide, methyl-2-propenyl and trisulphide, di-2-propenyl).
- The essential oil of *A. sativum* is endowed with a good inhibitory efficiency of up to 97.6% for a concentration of 1 g/L.
- EIS results show that the Nyquist diagrams obtained show two capacitive loops, one at high frequency which can be associated with the adsorption of a film on the surface of the copper, and the other at low frequency which can be attributed to the phenomenon of charge transfer at the copper/H₂SO₄ interface.

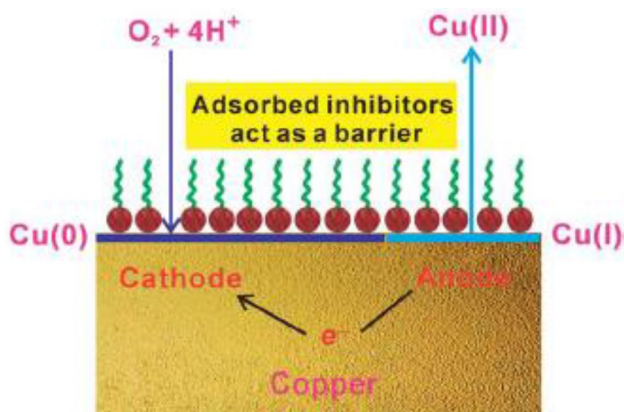


Fig. 8 Proposed scheme for the adsorption of inhibitor on the copper surface in acid medium

- The study of the temperature effect shows that our inhibitor has good inhibitory efficacy values in an ascending temperature range, which shows a good temperature resistance.
- The thermodynamic parameters confirm the physisorption of the studied inhibitor on the copper surface in 0.5M sulphuric acid media.
- SEM analysis coupled with EDX confirms the presence of a protective layer on the substrate surface.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Qiang Y, Zhang S, Xu S, Li W (2016) Experimental and theoretical studies on the corrosion inhibition of copper by two indazole derivatives in 3.0% NaCl solution. *J Colloid Interface Sci* 472:52–59. <https://doi.org/10.1016/j.jcis.2016.03.023>
2. Hegazy MA, Nazeer AA, Shalabi K (2015) Electrochemical studies on the inhibition behavior of copper corrosion in pickling acid using quaternary ammonium salts. *J Mol Liq* 209:419–427. <https://doi.org/10.1016/j.molliq.2015.05.043>
3. Dahmani K, Galai M, Cherkaoui M, El hasnaoui A, El Hessni A (2017) Cinnamon essential oil as a novel eco-friendly corrosion inhibitor of copper in 0.5M sulfuric acid medium. *JMES* 8(5):1676–1689
4. Tan B, Zhang S, Qiang Y, Guo L, Feng L, Liao C, Chen S (2018) A combined experimental and theoretical study of the inhibition effect of three disulfide-based flavouring agents for copper corrosion in 0.5M sulfuric acid. *J Colloid Interface Sci* 526:268–280. <https://doi.org/10.1016/j.jcis.2018.04.092>
5. Qiang Y, Zhan'g S, Guo L, Zheng X, Xiang B, Chen S, (2017) Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid. *Corros Sci* 119:68–78. <https://doi.org/10.1016/j.corsci.2017.02.021>
6. Quartarone G, Battilana M, Bonaldo L, Tortato T (2008) Investigation of the inhibition effect of indole-3-carboxylic acid on the copper corrosion in 0.5M H₂SO₄. *Corros Sci* 50(12):3467–3474. <https://doi.org/10.1016/j.corsci.2008.09.032>
7. Li H, Zhang S, Tan B et al (2018) Investigation of Losartan Potassium as an eco-friendly corrosion inhibitor for copper in 0.5M H₂SO₄. *J Mol Liq*. <https://doi.org/10.1016/j.molliq.2020.112789>
8. Antonijevic MM, Petrovic MB (2008) Copper corrosion inhibitors. A review. *Int J Electrochem Sci* 3:1–28
9. Khaled KF (2008) Adsorption and inhibitive properties of a new synthesized guanidine derivative on corrosion of copper in 0.5M H₂SO₄. *Appl Surf Sci* 255(5):1811–1818. <https://doi.org/10.1016/j.apsusc.2008.06.030>
10. Mihajlović MP, Antonijević MM (2015) Copper corrosion inhibitors. Period 2008–2014. A review. *Int J Electrochem Sci* 10:1027–1053
11. Zhang J, Zhang L, Tao G (2018) A novel and high-efficiency inhibitor of 5-(4-methoxyphenyl)-3h-1,2-dithiole-3-thione for copper corrosion inhibition in sulfuric acid at different temperatures. *J Mol Liq*. <https://doi.org/10.1016/j.molliq.2018.09.095>
12. Xu Y, Zhang S, Li W, Guo L, Xu S, Feng L, Madkour LH (2018) Experimental and theoretical investigations of some pyrazolo-pyrimidine derivatives as corrosion inhibitors on copper in sulfuric acid solution. *Appl Surf Sci* 459:612–620. <https://doi.org/10.1016/j.apsusc.2018.08.037>
13. Tan B, Zhang S, Qiang Y, Li W, Liu H, Xu C, Chen S (2019) Insight into the corrosion inhibition of copper in sulfuric acid via two environmentally friendly food spices: combining experimental and theoretical methods. *J Mol Liq*. <https://doi.org/10.1016/j.molliq.2019.110891>
14. Raja PB, Sethuraman MG (2008) Natural products as corrosion inhibitor for metals in corrosive media—a review. *Mater Lett* 62(1):113–116. <https://doi.org/10.1016/j.matlet.2007.04.079>
15. Fateh A, Aliofkhaezrai M, Rezvani AR (2017) Review of corrosive environments for copper and its corrosion inhibitors. *Arab J Chem* 13:481–544. <https://doi.org/10.1016/j.arabjc.2017.05.021>
16. Mo S, Luo H-Q, Li N-B (2016) Plant extracts as “green” corrosion inhibitors for steel in sulphuric acid. *Chem Pap*. <https://doi.org/10.1515/chempap-2016-0055>
17. Ajeigbe SO, Basar N, Hassan MA, Aziz M (2017) Optimization of corrosion inhibition of essential oils of *Alpinia galanga* on mild steel using response surface methodology. *J Eng Appl Sci* 12(9):2763–2771
18. Barakat Y, Hassan A, Paraka MA (1998) Corrosion Inhibition of mild steel in aqueous solution containing H₂S by some naturally occurring substances. *Materialwiss Werkstoffech* 9(7):365
19. Tiskar M, Galai M, EbnTouhami M, Satrani B, Ghanmi M, El Ammari Y, Chaouch A (2016) Inhibition of carbon steel Corrosion in Hydrochloric Solution with natural inhibitor case: Rosmarinus officinalis L. *Int J Acad Stud* 2(11):478–492
20. Benabida M, Galai M, Cherkaoui M, Dagdag O (2016) Potentials of nigella sativa oil as inhibition towards the corrosion of mild steel in neutral media. *Anal Bioanal Electrochem* 8(8):962–976
21. Tiskar M, Galai M, El Ammari Y, EbnTouhami M, Satrani B, Ghanmi M, Ettahir A, Chaouch A (2017) Chemical composition and inhibitory effect of *Artemisia herba-alba*'s essential oil on carbon steel corrosion in hydrochloric acid (1M). *Int J Acad Stud* 3(1):01–13
22. Tiskar M, Galai M, Elhadiri H, EbnTouhami M, Sfaira M, Satrani B, Ghanmi M, Chaouch A, Touir R (2016) *Juniperus phoenicea* essential oil as green corrosion inhibitor for mild steel in molar hydrochloric acid. *J Matér Tech* 104:609. <https://doi.org/10.1051/matech/2017003>
23. Piletta R, Zanettib M, Jungb G, Muneron de Mello JM, Dalcantonc F, Soaresa C, GracherRiellaa H, Antônio Fiori M (2019) Microencapsulation of garlic oil by β-cyclodextrin as a thermal protection method for antibacterial action. *Mater Sci Eng C* 94:139–149
24. Cardelle-Cobas A, Soria AC, Corzo-Martínez A, Villamiel M (2010) A comprehensive survey of garlic functionality. In: Pacurar M, Krejci G (eds) Book of garlic consumption and health publisher. Nova Science Publishers Inc., Hauppauge, pp 1–60. <https://doi.org/10.13140/2.1.4992.6728>
25. Al Mhyawi SR (2014) Corrosion inhibition of aluminum in 0.5M HCl by garlic aqueous extract oriental. *J Chem* 30(2):541–552. <https://doi.org/10.13005/ojc/300218>
26. Barreto LS, Tokumoto MS, Guedes IC, Melo HG, Amado FDR, Capelossi VR (2017) Evaluation of the anticorrosion performance of peel garlic extract as corrosion inhibitor for ASTM 1020 carbon steel in acidic solution. *Matéria (Rio de Janeiro)*. <https://doi.org/10.1590/s1517-707620170003.0186>
27. Yang B, Chen W, Mu DH (2014) Study of garlic extract as a green corrosion inhibitor for mild steel in acidic media. *Adv Mater Res* 960–961:118–125. <https://doi.org/10.4028/www.scientific.net/amr.960-961.118>

28. Devikala S, Kamaraj P, Arthanareeswari M, Patel MB (2019) Green corrosion inhibition of mild steel by aqueous *Allium sativum* extract in 3.5% NaCl. Mater Today Proc 14:580–589. <https://doi.org/10.1016/j.matpr.2019.04.182>
29. Afia L, Benali O, Salghi R, Ebenso Eno E, Jodeh S, Zougagh M, Hammouti B (2014) Steel corrosion inhibition by acid garlic essential oil as a green corrosion inhibitor and sorption behavior. Int J Electrochem Sci 9(2014):8392–8406
30. Satyal P, Craft JD, Dosoky NS, Setzer WN (2017) The chemical compositions of the volatile oils of garlic (*Allium sativum*) and wild garlic (*Allium vineale*). J Foods 6:63. <https://doi.org/10.3390/foods6080063>
31. Pyun MS, Shin S (2006) Antifungal effects of the volatile oils from Allium plants against Trichophyton species and synergism of the oils with ketoconazole. Phytomedicine 13:394–400
32. Douiri L, Boughdad A, Assobhei O, Moumni M (2013) Chemical composition and biological activity of *Allium sativum* essential oils against *Callosobruchus maculatus*. IOSR J Environ Sci Toxicol Food Technol 3:30–36
33. Romeilah RM, Fayed SA, Mahmoud GI (2010) Chemical compositions, antiviral and antioxidant activities of seven essential oils. J Appl Sci Res 6:50–56
34. Daouda Toure (2015) Etudes Chimique Et Biologique Des Huiles Essentielles De Quatre Plantes Aromatiques Medicinales De Côte D'ivoire. Chimie organique. Université Felix HouphouëtBoigny, Côte d'Ivoire, 2015. Français. fffNT: 29/2015ff. fffTel-01222964f
35. Boukhatem MN, Ferhat A, Kameli A (2019) Méthodes d'extraction et de distillation des huiles essentielles : revue de littérature. Rev Agrobiol 9(2):1653–1659
36. Satyal P, Craft J, Dosoky N, Setzer W (2017) The chemical compositions of the volatile oils of garlic (*Allium sativum*) and wild garlic (*Allium vineale*). Foods (Basel, Switzerland). <https://doi.org/10.3390/foods6080063>
37. Khaled KF (2008) Adsorption and inhibitive properties of a new synthesized guanidine derivative on corrosion of copper in 0.5M H₂SO₄. Appl Surf Sci 255(5):1811–1818. <https://doi.org/10.1016/j.apsusc.2008.06.030>
38. Quartarone G, Moretti G, Bellomi T, Capobianco G, Zingales A (1998) Using indole to inhibit copper corrosion in aerated 0.5M sulfuric acid. Corrosion 54(8):606–618. <https://doi.org/10.5006/1.3287636>
39. Wang DKY, Collier BAW, Macfarlane DR (1993) A kinetic model for the dissolution mechanism of copper in acidic sulfate solutions. Electrochim Acta 38:2121
40. Smyrl WH (1981) Comprehensive treatise of electrochemistry, vol 4. Plenum Press, New York, p 116
41. Kaesche H (1985) Metallic corrosion. NACE, Houston, p 124
42. Jinturkarp YC, Han KN (1998) Dissolution and corrosion inhibition of copper, zinc and their alloys. Corrosion 54(2):106–114
43. Tan B, Zhang S, Qiang Y, Feng L, Liao C, Xu Y, Chen S (2017) Investigation of the inhibition effect of Montelukast Sodium on the copper corrosion in 0.5 mol/L H₂SO₄. J Mol Liq 248:902–910. <https://doi.org/10.1016/j.molliq.2017.10.111>
44. El Faydy M, Galai M, EbnTouhami M, Obot IB, Lakhrissi B, Zarrouk A (2017) Anticorrosion potential of some 5-amino-8-hydroxyquinolines derivatives on carbon steel in hydrochloric acid solution: gravimetric, electrochemical, surface morphological, UV-visible, DFT and Monte Carlo simulations. J Mol Liq 248:1014–1027. <https://doi.org/10.1016/j.molliq.2017.10.125>
45. Qiang Y, Zhang S, Wang L (2019) Understanding the adsorption and anticorrosive mechanism of DNA inhibitor for copper in sulfuric acid. Appl Surf Sci. <https://doi.org/10.1016/j.apsusc.2019.06.190>
46. Ouakki M, Rbaa M, Galai M, Lakhrissi B, Rifi EH, Cherkaoui M (2018) Experimental and quantum chemical investigation of imidazole derivatives as corrosion inhibitors on mild steel in 1.0 M hydrochloric acid. J Bio Tribo Corros 4:35
47. Kadiri L, Galai M, Ouakki M, Essaadaoui Y, Ouass A, Cherkaoui M, Rifi EL, Lebkiri A (2018) J Anal Bioanal Electrochem 10(2):249–268
48. Cruz J, Martínez R, Genesca J, Ochoa E (2004) Experimental and theoretical study of 1-(2-ethylamino)-2-methylimidazoline as an inhibitor of carbon steel corrosion in acid media. J Electroanal Chem 566:111
49. Bentiss F, Traisnel M, Vezin H, Lagrenée M (2003) Linear resistance model of the inhibition mechanism of steel in HCl by triazole and oxadiazole derivatives: structure–activity correlations. Corros Sci 45:371
50. Jmiai A, El Ibrahim B, Tara A, El Issami S, Jbara O, Bazzi L (2018) Alginate biopolymer as green corrosion inhibitor for copper in 1 M hydrochloric acid: experimental and theoretical approaches. J Mol Struct 1157:408–417. <https://doi.org/10.1016/j.molstruc.2017.12.060>
51. Rehim SSA, Hassan HH, Amin MA (2002) Corrosion and corrosion inhibition of Al and some alloys in sulphate solutions containing halide ions investigated by an impedance technique. Appl Surf Sci 189:279
52. M'hanni N, Galai M, Anik T, EbnTouhami M, Rifi EH, Asfari Z, Tourir R (2017) Influence of additives selected calix [4] arenes on electroless copper plating using hypophosphite as reducing agent. Surf Coat Technol 310:8–16
53. Galai M, Ouassir J, EbnTouhami M, Nassali H, Benqlilou H, Belhaj T, Berrami K, Mansouri I, Oauki B (2017) α -Brass and $(\alpha + \beta)$ brass degradation processes in azrou soil medium used in plumbing devices. J Bio Tribo Corros 3:30
54. Zheng X, Zhang S, Li W, Yin L, He J, Wua J (2014) Investigation of 1-butyl-3-methyl-1H-benzimidazolium iodide as inhibitor for mild steel in sulfuric acid solution. Corros Sci 80:383
55. Rahmouni K, Keddami M, Srhiri A, Takenouti H (2005) Corrosion of copper in 3% NaCl solution polluted by sulphide ions. Corros Sci 47:3249–3266
56. Kardas G (2005) The inhibition effect of 2-thiobarbituric acid on the corrosion performance of mild steel in HCl solutions. J Mater Sci 41:337
57. Essaadaoui Y, Galai M, Ouakki M, Kadiri L, Ouass A, Cherkaoui M, Rifi E, Lebkiri A (2019) Study of the anticorrosive action of eucalyptus camaldulensis extract in case of mild steel in 1.0 M HCl. J Chem Technol Metall 54(2):431–442
58. Deyab MA (2015) Egyptian licorice extract as a green corrosion inhibitor for copper in hydrochloric acid solution. J Ind Eng Chem 22:384–389. <https://doi.org/10.1016/j.jiec.2014.07.036>
59. Deyab MA (2013) Effect of halides ions on H₂ production during aluminum corrosion in formic acid and using some inorganic inhibitors to control hydrogen evolution. J Power Sources 242(2013):86
60. Deyab MA (2007) Effect of cationic surfactant and inorganic anions on the electrochemical behavior of carbon steel in formation water. Corros Sci 49(2007):2315
61. Ouakki M, Galai M, Cherkaoui M, Rifi E, Hatim Z (2018) Inorganic compound (Apatite doped by Mg and Na) as a corrosion inhibitor for mild steel in phosphoric acidic medium. Anal Bioanal Electrochem 10(7):943–960
62. Rbaa M, Galai M, El Kacimi Y, Ouakki M, Tourir R, Lakhrissi B, EbnTouhami M (2017) Adsorption properties and inhibition of carbon steel corrosion in a hydrochloric solution by 2-(4,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)-5-methoxyphenol, Portugaliae. Electrochim Acta 35(6):323–338
63. Dkhireche N, Galai M, El Kacimi Y, Rbaa M, Ouakki M, Lakhrissi B, EbnTouhami M (2018) New quinoline derivatives as sulfuric acid inhibitor's for mild steel. Anal Bioanal Electrochem 10(1):111–135

64. Hong S, Chen W, Lao HQ, Li NB (2012) Inhibition effect of 4-amino-antipyrine on the corrosion of copper in 3 wt.% NaCl solution. *Corros Sci* 57:270
65. Nabah R, Benhiba F, Ramli Y, Ouakki M, Cherkaoui M, Oudda H, Tourir R, Warad I, Zarrouk A (2018) Corrosion inhibition study of 5, 5-diphenylimidazolidine-2, 4-dione for mild steel corrosion in 1 M HCl solution: experimental, theoretical computational and Monte Carlo simulations studies. *Anal Bioanal Electrochem* 10(10):1375–1398
66. Oguzie EE (2008) Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel. *Corros Sci* 50:2993
67. Oguzie EE, Onuoha GN, Onuchukwu AL (2005) Inhibitory mechanism of mild steel corrosion in 2 M sulphuric acid solution by methylene blue dye. *Mater Chem Phys* 89:305
68. Mistry BM, Patyl NS, Sahoo S, Junhari S (2012) Experimental and quantum chemical studies on corrosion inhibition performance of quinoline derivatives for MS in 1N HCl. *Bull Mater Sci* 35:459–469
69. Guo L, Dong W, Zhang S (2014) Theoretical challenges in understanding the inhibition mechanism of copper corrosion in acid media in the presence of three triazole derivatives. *RSC Adv* 4:41956
70. Khaled KF, Amin MA (2009) Dry and wet lab studies for some benzotriazole derivatives as possible corrosion inhibitors for copper in 1.0 M HNO₃. *Corros Sci* 51:2098–2106

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