SYNERGISTIC EFFECT OF BACL2 ON CORROSION INHIBITION OF COPPER BY *MENTHA SPICATA* OIL IN 1M NITRIC ACID: GRAVIMETRIC AND RAMAN SPECTROSCOPY STUDIES

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Abstract. The effect of *Mentha Spicata* oil and the mixture of BaCl$_2$ and *Mentha Spicata* oil on corrosion of copper in 1M HNO$_3$ have been investigated using weight loss methods and Raman spectroscopy. The study revealed that copper is more efficiently inhibited by *Mentha Spicata* oil in the presence of BaCl$_2$ than pure oil. The inhibition efficiencies increased with increased concentration of the additives. The highest inhibition efficiency of 56.12 % was observed with single *Mentha Spicata* oil. An improved inhibition efficiency of 75.13 % was observed with the mixture of *Mentha Spicata* oil and BaCl$_2$ at 298 K in 1M HNO$_3$, an effect attributed to synergism between *Mentha Spicata* oil and BaCl$_2$. Inhibition efficiency decreased with increase in temperature from 298–328 K. The adsorption of inhibitor molecules on metal surface followed Frumkin and Langmuir isotherm. Thermodynamic parameters such as enthalpy ΔH, free energy of adsorption ΔG and entropy of adsorption are obtained from experimental temperatures ranging from 298–328 K. Raman Spectroscopy and mapping were used to characterize the surface layers.
Keywords: corrosion, copper, *Mentha Spicata* oil, inhibitors, acid medium, synergism.

1. Introduction

Copper metal is considered one of the most important metals resistant to corrosion, so its strong presence is noted in industrial structures and even in the means of daily human use, which ranked it among the important metals in the world.[1-6] However, many acids attack it quite easily[7] due to their uses in stripping or cleaning and removing localized deposits (unevenly distributed scale, rust, bacterial deposits, *etc.*). The aggressiveness of these acidic solutions leads to the use of inhibitors which is the most widely used method[8-10] in acidic media[11,12] in order to limit the attack on metallic materials.[7-10,13]

Inhibitors are chemical compounds that are added in small quantities to the corrosive medium and lead to stopping or slowing down the corrosion. They are of two types, either mineral or organic,[8] and the latter is the most used and has gained great importance in the recent times due to their good results in inhibition.[13-15]

Current researches are increasingly directed towards the development of non-toxic and stable organic molecules. The use of plant extracts, as corrosion inhibitors, is a topic of research in development. Indeed, these natural extracts contain many families of natural organic compounds (flavonoids, alkaloids, tannins, *etc.*), which are "ecological", easily available, and renewable.[16] The efficiency of these inhibitors is sometimes improved by the addition of some other compounds which act in synergism.

Mint is a plant with a pleasant smell; it has been used since ancient times in alternative medicine as a sedative and in solving many digestive problems. Mint extract was used in the corrosion protection of carbon steel in 1M HCl solution,[17-22] corrosion of mild steel in 1M HCl,[23] corrosion of Aluminum in 1 molar hydrochloric acid,[24] mild steel in 0.5M H$_2$SO$_4$ [25] using electrochemical techniques and weight loss. In these studies, it was found to be a very good inhibitor with an efficacy reaching around 97 %.[26] In this paper, we have evaluated, by gravimetric measurements, the inhibitory efficiency of the essential oil of mint vis-a-vis the corrosion of copper in 1M nitric acid medium HNO$_3$ and studied its synergistic effect with BaCl$_2$. In order to access

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the composition of the deposited film, the study was completed by a characterization of the surface by Raman spectroscopy.

2. Experimental

2.1. Materials

Mentha spicata was collected in May 2020 from Beloul 40 km far from Saïda (868 (m), 34° 502 003 N, 0° 092 003 E) in the west northern region of Algeria. Voucher specimen was identified by Pr Nouri BENABADJI of Department of Biology-University of Tlemcen, Algeria and deposited in the institutional herbarium. The plants were cut at ground surface and taken to laboratory to extract essential oil. Chopped plants were used fresh for determination of essential oil content by hydro distillation method using Clevenger type apparatus at 333 K for 3 h. The essential oil was dried with anhydrous sodium sulfate, stored at 269 K and used for GC-MS analysis. The essential oil content (%) was determined on fresh weight basis as an average of three samples. The identification of the oil is performed by Allali *et al.*[27]

The metal used in this study is the commercial copper of 99.9 % purity. The copper samples were pre-treated prior to the experiments by grinding with emery paper until to 1200 grade; rinsed with distilled water, degreased in acetone, washed again with distilled water and then dried at room temperature before use. The aggressive solutions of 1M HNO_3 were prepared by dilution of analytical grade 67 % HNO_3 with double distilled water.

Inhibitor were dissolved in acid solution at the required concentrations (in g/L), and the solution in the absence of inhibitor was taken as blank for comparison purposes. The test solutions were freshly prepared before each experiment by adding *M. Spicata* oil directly to the corrosive solution. Experiments were conducted on several occasions to ensure reproducibility. Concentrations of *M. Spicata* oil were 0.5, 1, 1.5, 2, and 2.5 g/L. The synergistic impact of chloride ions was studied by introducing $5 \cdot 10^{-3}$ M $BaCl_2$.

Raman spectra were measured using a HORIBA LABRAM HR Raman spectrometer operated in single spectrograph mode with a holographic dispersive grating of 600 grooves/mm.

The samples were analyzed in the back-scattering mode on the microscope stage of an Olympus confocal microscope attached to the spectrometer using a long working distance 50× objective. The detector used was a liquid nitrogen cooled charge coupled device Symphony IGA detector. A 663 nm holographic notch filter was used to remove the Rayleigh-scattered light.

The entrance slit width was 100 µm giving a resolution of 2 cm⁻¹ in the range between 100 and 5000 cm⁻¹. Repeated acquisition using the highest magnification were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer.

2.2. Weight loss measurements

This method has the advantage of being easy to implement, and of not requiring significant equipment, its principle is based on the measurement of the loss in weight (*Δm*) undergone by a sample of surface S, for a time t immersion in a corrosive solution at constant temperature. The mass loss tests were carried out in a 250 mL beaker. A water bath (Wise) was used to allow the electrolyte to be maintained at the desired temperature. Weight-loss experiments were conducted on copper coupons with a surface area of 7.6 cm².

Experiments on copper plates immersed in solutions of nitric acid of concentration 1 mol·L⁻¹, without and with the addition of different concentrations of inhibitor and $5 \cdot 10^{-3}$ mol·L⁻¹ $BaCl_2$, under 6 hours of immersions and with varying temperatures from 298 K to 328 K were performed.

The corrosion rate is calculated by the following formula:

$$W = \Delta M / S \cdot t \qquad (1)$$
$$\Delta M = M_1 - M_2 \qquad (2)$$

where ΔM represents the difference between the initial mass M_1 and the final mass M_2 after a time *t* equal to 6 h. S is the surface of the metal exposed to the study solution.

This value of the corrosion rate is the average of three tests carried out under the same conditions for each concentration. The value of inhibitory efficacy is given by the following formula:

$$E\% = 100 \cdot \frac{W_0 - W}{W_0} \qquad (3)$$

where W_0, W respectively represent the corrosion rates of copper in the absence and in the presence of the inhibitor.

2.3. Raman spectroscopy

Many reference works on the atmospheric corrosion of copper developed the theory on the formation of copper sulfates and, more particularly the difference in formation of antlerite and brochantite. More information can be found in the literature.[28-30]

The corrosion products formed on the surface of the samples were analyzed using Raman spectroscopy technique. Raman spectra were obtained before and after immersion of copper in solutions of: 1M HNO_3 and 1M HNO_3 containing: 2.5 g/L M.E.O, 2.5 g/L M.E.O + + $5 \cdot 10^{-3}$M $BaCl_2$ for 24 h.

The idea is on the one hand to use Raman to detect the presence of oxides after immersion of copper in a corrosive medium and on the other hand to have copper sheets mapped in order to see the distribution of the corroded zones by compared to inhibited zones.

3. Results and Discussion

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration

The variation in the mass loss (Δm) of copper expressed in (mg) in HNO_3 medium at 6 hours of immersion time at different concentrations (From 0.5 g/L to 2.5 g/L) was studied in the absence and in the presence of inhibitor at 298 K. It makes it possible to determine the corrosion rate (W) expressed in ($mg \cdot cm^{-2} \cdot h^{-1}$), the rate of surface coverage (θ) and to calculate the inhibitory efficiency of M.E.O (IE %). The results obtained are summarized in Table 1.

We can see from the measured data that increasing the essential oil concentration increases surface coverage (θ) and thus IE%, but decreases corrosion rate (W_{corr}). The highest level of inhibition is 56.12 % at 2.5 g/L of the concentration of inhibitor. This implies that increasing the concentration of essential oil on the copper surface raises the amount of inhibitor molecules adsorbed on the surface and decreases the surface area available for direct acid attack on the metal surface.

The results also show that M.E.O alone cannot effectively protect the corrosion of the metal in 1M nitric acid so we have tried to improve its inhibition efficiency by adding halide ions such as chloride which may help the inhibitor to adsorb better to the metal surface.[31,32]

3.1.2. Synergistic study

We are going to study the effect of $BaCl_2$ on the inhibition efficiency of *Mentha Spicata* essential oil in nitric acid medium (1M). This step is carried out at different concentrations of M.E.O (from 0.5 to 2.5 g/L) with the addition of $5 \cdot 10^{-3}$ M of $BaCl_2$. Table 2 gives values of the inhibition efficiency for the corrosion of copper in 1M HNO_3 after addition of $5 \cdot 10^{-3}$ M of $BaCl_2$ at different concentrations of M.E.O.

We note that the addition of $BaCl_2$ to the acidic medium HNO_3 1M in the presence of menthol essential oil leads to a decrease in the corrosion rate and therefore it actually increases significantly the inhibitory efficiency of M.E.O (75.13 %). These results clearly demonstrate the synergistic effect between Cl ions and M.E.O.

3.1.2.1. Comparison of inhibitory efficiencies and synergy

In order to clearly illustrate the role of synergy, *i.e.*, the effect of chloride ions on the corrosion of copper in 1M HNO_3 in the presence of M.E.O, we carried out this comparison between the inhibitory efficiencies with respectively single M.E.O and M.E.O + $BaCl_2$ through histograms (Fig. 1).

Table 1. Values of the inhibitory efficacy of M.E.O at different concentrations in 1M HNO_3obtained by gravimetry at 298 K (6 hours of immersion)

Concentration (g/L)	W_{corr} / ($mg \cdot cm^{-2} \cdot h^{-1}$)	IE / %	θ (Surface Coverage)
Blank	0.0620	------	------
0.5	0.0470	24.09	0.24
1	0.0420	32.25	0.322
1.5	0.0375	39.51	0.395
2	0.0354	42.90	0.429
2.5	0.0272	56.12	0.561

Table 2. Inhibition efficiency for different concentrations of M.E.O on copper in 1M HNO_3 in the presence of $5 \cdot 10^{-3}$ M of $BaCl_2$ at 298 K

Concentration(g/L)	W_{corr} / ($mg \cdot cm^{-2} \cdot h^{-1}$)	IE / %	θ (SurfaceCoverage)
Blank	0.0620	------	---------
0.5	0.0348	43.97	0.439
1	0.0282	54.46	0.544
1.5	0.0273	55.83	0.558
2	0.0161	73.95	0.739
2.5	0.0154	75.13	0.751

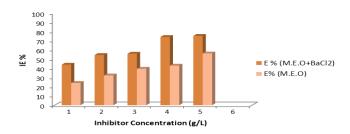**Fig. 1.** Comparison between the inhibitory efficiencies M.E.O alone and (M.E.O + 5·10⁻³ M BaCl₂)

From this histogram (Fig. 1), it can be clearly seen that the presence of $BaCl_2$ in the solution containing (HNO_3 + M.E.O) considerably influences the inhibitory efficiencies, for example, for the concentration of 2.5 g/L, we have an inhibitory efficacy rate of 56.12 % while in the presence of the chloride ions we have 75.13 %. This shows the existence of a beneficial synergistic effect between M.E.O and $BaCl_2$.

3.1.2.2. Synergism parameter

The synergism parameters S are determined from the mathematical equation proposed by Aramaki and Hackerman:[33,34]

$$S = (1 - P_{1+2})/(1 - P'_{1+2}) \qquad (4)$$
$$P_{1+2} = (P_1 + P_2) - (P_1 \cdot P_2) \qquad (5)$$

where P_1 represents the inhibition efficiency of M.E.O, P_2 is that of $BaCl_2$, and P'_{1+2} is the measured inhibition efficiency for M.E.O and $BaCl_2$ together.

The values of the calculated S are given in the following Table 3.

Table 3. Values of synergisms parameter for different concentrations of M.E.O and 5·10⁻³ M of BaCl₂

Concentration (g/L)	Synergism parameter
0.5	0.55
1	0.61
1.5	0.56
2	0.90
2.5	0.72

It can be seen from this table that all values are less than unity. This result suggests that the improvement of inhibition efficiency generated by the addition of $BaCl_2$ to M.E.O is generally due to a competitive adsorption between M.E.O and $BaCl_2$.

It is important to emphasize that Aramaki[33,34] explained the synergistic effect either by competitive adsorption or by cooperative adsorption between the two compounds. In the first case, the two compounds are adsorbed on different sites on the surface of the electrode, while in the second case, one is chemisorbed on the surface of the metal and the other is physisorbed on it. If $S<1$, we are in the presence of competitive adsorption. If, on the other hand, $S>1$, cooperative adsorption occurs. In this study, values less than 1 show that we are in the presence of competitive adsorption.

3.1.3. Temperature Effect

Temperature is one of the factors that can affect both the behavior of the inhibitor, either in its form or in the way it adsorbs or desorbs to the copper surface. In general, temperature has an important effect on corrosion phenomena; the increase in temperature accelerates the corrosion phenomena, because it decreases the domains of stability of metals and accelerates the kinetics of reactions and transport. Singh *et al.* consider that the increase in temperature produces an increase in electron density around the adsorption centers.[34]

Also, the corrosion rate increases when the temperature increases. However, the extent of its influence differs depending on the corrosive environment in which the material is found.[35] In order to know the influence of the temperature on the evolution of the corrosion, we carried out a series of measurements keeping the same operating parameters.

We conducted gravimetric measurements on copper in HNO_3 1M in the absence and presence of various additives, in the temperature range of 298–328 K, which we present in Table 4.

As can be seen from Fig. 2, the inhibitory efficacy values for M.E.O alone decrease with increasing temperature. However, these values increase with increasing temperature in the existence of $BaCl_2$. As a result, the addition of $BaCl_2$ significantly improved the efficiency of M.E.O inhibition at all temperatures.

Ivanov considers the increase in (EI) with temperature as the change in the nature of the mode of adsorption; the inhibitor is physisorbed at low temperatures, while chemisorption is promoted as the temperature increases.[26,36]

Table 4. Effect of temperature on the inhibition efficiency (E %)

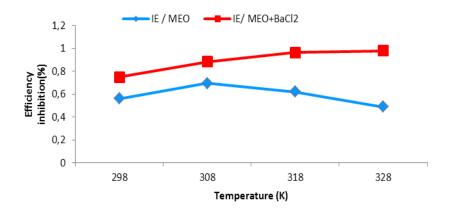| T (K)	M.E.O (2.5 g/L)			M.E.O (2.5 g/L)+ 5·10⁻³ M BaCl₂		
	W_{0corr}	W_{corr}	$E / \%$	W_{0corr}	W_{corr}	$E / \%$
298	0.0620	0.0272	56.12	0.0620	0.0154	75.13
308	0.3070	0.0930	69.70	0.3070	0.0359	88.30
318	1.4831	0.5632	62.02	1.4831	0.0521	96.48
328	7.3941	3.7659	49.06	7.3941	0.1551	97.90

Fig. 2. Variation of the inhibitory efficiency as a function of temperature

3.1.4. The activation parameters

The Arrhenius equation is used to account for the effect of temperature (T) on the corrosion rate and therefore considers that the logarithm of the corrosion rate W_{corr} is a linear function of T^{-1} (Eq. 6):[37,38]

$$\ln w = (-E_a/RT) + A \qquad (6)$$

where w represents the corrosion rate calculated from gravimetric measurements, A represents the Arrhenius frequency factor, R represents the molar gas constant, and T represents the absolute temperature.

Fig. 3 shows the Arrhenius coordinate plot of the copper corrosion rate in HNO₃ 1M in the absence and presence of inhibitors.

We notice from this figure that the curves ln $W_{corr} = f(1/T)$ gives linear lines so they follow the Arrhenius law. We can therefore calculate the activation energies from the Arrhenius relation. The activation energies for the various concentrations without and with addition of inhibitors are given in Table 5.

Table 5. Activation energy for dissolving copper in 1M HNO₃ alone and in the presence of inhibitors

Inhibitor	E_a (kJ·mol⁻¹)
Blank	129
M.E.O	134
M.E.O + BaCl₂	59

The calculations show that E_a increases in the presence of M.E.O (134 kJ/mol) but decreases in the presence of the mixture M.E.O+BaCl₂ (59 kJ/mol).

The higher E_a value observed in the presence of 2.5 g/L M.E.O suggests that a higher energy barrier is needed for the corrosion reaction to occur[39] while the lower value observed after addition of 5·10⁻³ M BaCl₂ is related to the higher adsorption of the mixture (M.E.O+BaCl₂) on the copper surface, which is primarily due to strong chemical interaction.[26,40,41]

An alternative formula of the Arrhenius equation (6) allows to determine the enthalpy and the entropy of activation according to the following equation:[42,43]

$$W = \frac{RT}{Nh} exp\left(\frac{\Delta Sa}{R}\right) \exp\left(-\frac{\Delta Ha}{RT}\right) \qquad (7)$$

where h is Planck's constant, N is Avogadro's number, ΔH_a° is the change in enthalpy of activation, and ΔS_a° is the change in entropy of activation.

The variation of $\ln(W/T)$ as a function of the inverse of the temperature is a straight line (Fig. 4), with a slope of ($-\Delta H_a^\circ/R$) and an ordinate at the origin equal to ($\ln R/Nh + \Delta S_a^\circ/R$).[42]

We can therefore calculate the values of ΔH_a° and ΔS_a°. The values of the enthalpies ΔH_a° and of the entropies ΔS_a° are given in Table 6.

Table 6. Enthalpy ΔH_a° and entropy ΔS_a° of activation for copper in 1M HNO₃ in the absence and presence of inhibitors

Inhibitor	ΔH_a° (kJ/mol)	ΔS_a° (J/mol)
Blank	126.69	156.701
M.E.O	131.814	165.482
M.E.O + BaCl₂	56.583	-89.9187

From these results we can draw information on the mechanism of inhibition of copper corrosion. The positive signs of enthalpy ΔH_a° reflect the endothermic nature of the copper dissolution process.[37,38,44] The increase in adsorption enthalpy in the case of single M.E.O corresponds to a decrease in metal dissolution.

In the presence of single M.E.O the value of ΔS_a° increases and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes.[45]

The negative value of the standard entropy ΔS_a° in the presence of BaCl₂ reflects a reduction in the disorder that occurs during the formation of the complex metal / adsorbed molecules.[46]

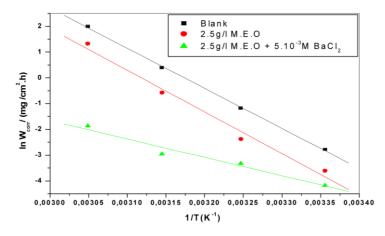**Fig. 3.** ln W_{corr} *vs.* $1/T$ for copper in 1M HNO$_3$ in the absence and
in the presence of 2.5 g/L M.E.O and 2.5g/L M.E.O + 5·10^{-3}M BaCl$_2$
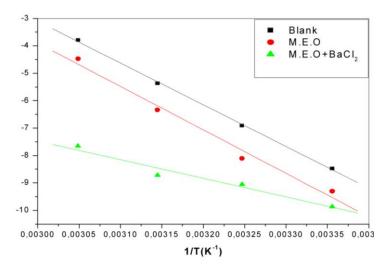

Fig. 4. Plots of ln (W/T) *vs.* $1/T$ for copper in 1M HNO$_3$ in the absence
and in the presence of M.E.O and M.E.O + BaCl$_2$

3.1.5. Adsorption isotherm and Thermodynamic parameters

The inhibition of corrosion of metals by organic compounds is explained by their adsorption on the metal surface. Adsorption isotherms are then an important complement capable of determining the electrochemical mechanism that leads to the adsorption of these organic compounds to the surface. To identify the type of adsorption corresponding to this study, different types of isotherms were tested: Langmuir, Temkin, Frumkin, Frundlich, and Flory Huggins using the data of Tables 1 and 2. The coefficient (R^2) was used to select the proper isotherm. It is noted that the linear correlation coefficients are close to 1. The Frumkin isotherm provides the most accurate fit for M.E.O alone and Langmuir isotherm the best fit for M.E.O with addition of BaCl$_2$ in 1M nitric acid. Figs. 5 and 6 represent the adsorption isotherms plotted at 298 K from the values obtained from the gravimetric measurement. According to these isotherms, the recovery rate (θ) is related to the concentration of inhibitor by the following equations:

Frumkin adsorption isotherm:

$$\ln \left(\frac{\theta}{(1-\theta) \times C}\right) = lnK_{ads} + 2a\theta \qquad (8)$$

Langmuir adsorption isotherm:

$$\frac{Cinh}{\theta} = \frac{1}{Kads} + Cinh \qquad (9)$$

The adsorption constant K_{ads} is related to the standard free adsorption energy ΔG_{ads} by the following equation:[40,47]

$$\Delta G^{\circ}_{ads} = -RTln(K_{ads} \times 55.5) \qquad (10)$$

R is the gas constant, T is the temperature, and 55.5 is the concentration of the water in the solution in mol·L^{-1}, and T is the temperature in Kelvin.[48]
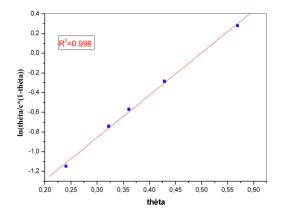
Fig. 5. Frumkin adsorption isotherm for copper immersed in 1M nitric acid with addition of M.E.O
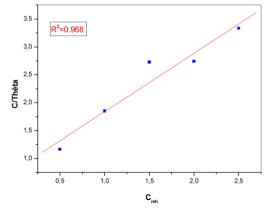

Fig. 6. Langmuir adsorption isotherm for copper immersed in 1M nitric acid with addition of (M.E.O + BaCl₂)

The values of the free energy of adsorption as calculated from Eq. (10) in the absence and the presence of BaCl₂ are -11.86 and -17.69 kJ/mol, respectively.

Negative values of $\Delta G°_{ads}$ indicate the spontaneity of the adsorption process and the stability of the adsorbed layer on the metal surface.[49] Generally, the values of $\Delta G°_{ads}$, around -20 kJ·mol⁻¹ or less negative, are linked to electrostatic interactions between charged molecules and the metal (physical adsorption), at this level the inhibition activity is mainly dominated by coulombic interactions,[14] while those close to -40 kJ·mol⁻¹ or more negative involve a charge transfer between the organic molecules and the metal surface (chemisorption).[50,51]

The values of $\Delta G°_{ads}$ obtained in this investigation are close to -20 KJ.mol⁻¹ in both cases, suggesting that single M.E.O and M.E.O + BaCl₂ are physisorbed on the surface of metal, which results in electrostatic interactions between the surface of the metal and the film formed. The increase in the values of $\Delta G°_{ads}$ in the presence of BaCl₂ indicates stronger interaction of the inhibitor molecules with the metal surface in the presence of chloride ions.[52]

3.2. Raman Spectroscopy analysis

The Electronic Microscopy of the Raman (Fig. 7) of the surfaces of copper samples were taken at same magnification to see the changes that occurred during corrosion process in the absence and presence of mint essential oil at 2.5 g/L during 24 h at 303 K.
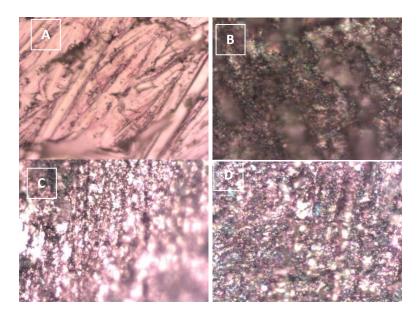

Fig. 7. Raman Electronical microscopy morphologies of (**A**) copper (**B**) in 1M HNO₃ and (**C**) 1M HNO₃ + 2.5 g/L *Mint Oil* and (**D**) 1M HNO₃ + 2.5 g/L *Mint Oil with BaCl₂* **for** 24 h immersion (magnification *100)

The EM image of the copper specimen in the absence of the inhibitor (Fig. 7B) shows an irregular and damaged surface owing to rapid corrosion attack if we compare that with pure copper (Fig. 7A). However, a relatively smoother and less corroded morphology of copper surface can be observed in the presence of inhibitor (Fig. 7C), this effect is improving in presence of $BaCl_2$ (Fig. 7D). This may be intercepted by the adsorption of molecules of this inhibitor on the electrode surface. It is thought that the molecules of inhibitor depress the corrosion by the formation of an adherent deposit on the electrode surface limiting the access of the electrolyte to the surface of the copper. This result confirms those from weight loss and electrochemical measurements.

Fig. 8 show the Raman spectra of copper, three characteristic peaks of Cu_2O are observed at 97, 147, 615 cm^{-1} in the spectrum of copper plates. The Raman microscope make possible to do spectra by targeting the oxidized parts and the pure parts. We observe in the zone (A) the characteristic spectrum of copper with two peaks 615 cm^{-1}, for the oxidized zones (B) we observe the appearance of peaks at 1370 and 1578 cm^{-1} corresponding to D and G bands due to the deposition of a thin layer of cuprite (Cu_2O) on the surface on areas not inhibited by essential oils, these two peaks are observed in the presence of $BaCl_2$ but with a very low intensity.[53]

We provide a Raman mapping of our copper plates which were put in an aggressive 1M HNO_3 medium in the presence of inhibitor with and without $BaCl_2$ (Fig. 9). These maps will allow us to see the distribution of the corroded parts on the copper plate and to see the effect of the inhibitor by delimiting the areas having been attacked by the acid and the areas inhibited by our essential oil.
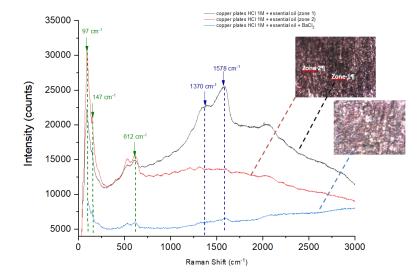

Fig. 8. Raman spectra of copper 1M HNO_3 + 2.5 g/L Mint Oil (zone 1), copper 1M HNO_3 + 2.5 g/L Mint Oil (zone 2) and copper 1M HNO_3 + 2.5 g/L Mint Oil+$BaCl_2$
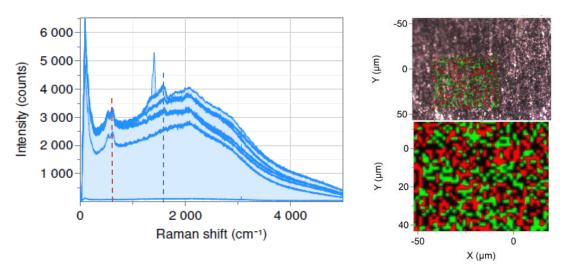

Fig. 9. Raman mapping of copper plates in HNO_3 1M + Mint essential oil
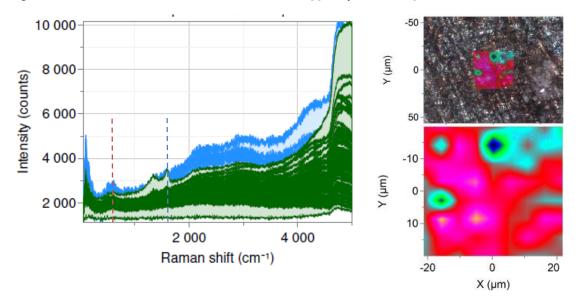
Fig. 10. Raman mapping of copper plates in HNO₃ 1M + Mint essential oil and BaCl₂

The Electronic Microscopy morphology of copper in HNO₃ and MEO shows two different kind of area. We have chosen an area comprising the two colors of our copper plate with a number of points to make our mapping of 164 in order to have a number of Raman spectra covering the entire area. The spectra show the presence of two spectra the first areas for which we have chosen a red color and a second area corresponding to the appearance of the peaks at 1370 and 1578 cm^{-1} corresponding to D and G bands due to the deposition of a thin layer of carbon. If we compare the distribution of the two given zones compared to the results obtained by gravimetry, we observe the same ratio which corresponds to 56 % of inhibition (Fig. 10).

As shown by gravimetry, the presence of BaCl₂ increases the inhibition rate to 75 %, this increase is reflected in the Raman mapping by an increase in the copper zone given by the red color and a decrease in the bands given in blue color, this result shows the increase of the inhibitory effect in the presence of BaCl₂ and confirms the results obtained by gravimetry.

4. Conclusions

We carried out a study on the evaluation of the inhibitory power of menthol essential oil on copper corrosion in HNO₃ 1M medium using the gravimetric method and Raman spectroscopy.

■   The work performed on M.E.O revealed that this inhibitor has a moderate inhibitory potency against copper corrosion in 1M HNO₃ medium, which increases with increasing concentration to reach a maximum value of 56.12 % at 2.5 g/L.

■   The addition of BaCl₂ at increasing concentrations of the inhibitor resulted in a decrease in corrosion rates; this decrease is accompanied by an increase in inhibitory efficiencies to reach a maximum value of 75.13 % at the concentration of 2.5 g/L, therefore the addition of BaCl₂ enhances the inhibition performance of the M.E.O in 1 M HNO₃ solution.

■   The increase in temperature affects the inhibitory effectiveness.

■   The synergism parameter suggests that there is a competitive mechanism between the chloride ions and M.E.O.

■   The adsorption of M.E.O alone and in combination with chloride ions obeys Frumkin and Langmiur adsorption isotherms, respectively.

■   Negative values of the activation enthalpy indicate the spontaneity of the adsorption process and that the copper dissolution is endothermic.

■   The thermodynamic parameters calculated from the adsorption isotherms showed that physisorption is involved in the inhibition process.

■   Raman Spectra and Raman Mapping confirm the results obtained by gravimetry and the use of this method shows a new possibility in the treatment of the results of corrosion inhibition, the mapping shows very well the distribution of the corroded parts compared to the parts inhibited by MEO with an increase of the inhibition in the presence of BaCl₂.

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СИНЕРГІЧНИЙ ЕФЕКТ BaCl₂ НА ІНГІБУВАННЯ ОЛІЄЮ *Mentha Spicata* КОРОЗІЇ МІДІ В 1М НІТРАТНІЙ КИСЛОТІ: ГРАВІМЕТРИЧНЕ ТА РАМАН-СПЕКТРОСКОПІЧНЕ ДОСЛІДЖЕННЯ

Анотація. *За допомогою методів втрати ваги та наман-спектроскопії досліджено вплив суміші олії Mentha Spicata та суміші BaCl₂ й олії Mentha Spicata на корозію міді в 1М HNO₃. Дослідження показало, що олія Mentha Spicata ефективніше інгібує мідь у присутності BaCl₂ порівнянj з самою олією. Ефективність інгібування збільшувалась із підвищенням концентрації добавок. З використанням самої лише олії Mentha Spicata dslpyfxtyj найвищу ефективність інгібування 56,12 %. Підвищену ефективність інгібування 75,13 % спостерігали для суміші олії Mentha Spicata і BaCl₂ за 298 К в 1М HNO₃; цей ефект пояснюється синергізмом між олією Mentha Spicata і BaCl₂. Ефективність інгібування знижувалася з підвищенням температури від 298 до 328 К. Адсорбція молекул інгібітора на поверхні металу відповідала ізотермі Фрумкіна та Ленгмюра. Термодинамічні параметри, такі як ентальпія ΔH, вільна енергія адсорбції ΔG та ентропія адсорбції, були отримані з експериментальних температур у діапазоні 298–328 К. Для дослідження поверхневих шарів використовували Раман-спектроскопію та мапінг.*

Ключові слова: *корозія, мідь, олія Mentha Spicata, інгібітори, кисле середовище, синергізм.*