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The Nigella Sative and Elettaria Cardamomum oils as an Environment-Friendly inhibitor on the Corrosion of Brass in 1M HCl

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ABSTRACT

The purpose of this research is to find a new easy inhibitors preparation and easy to prepare, non-toxic, not cheap and abundant. In this study, we of essential oils extracted from the seeds of Nigella Sativa and Elettaria Cardamomum to protect the copper alloy-. Zinc corrosion in the center (brass) erosive solution for one molar hydrochloric acid HCl 1M. The results of the polarization curves show that the corrosion current density decreases 0.204 mA/cm^2 to 0.042 mA/cm^2 and to 0.056 mA/cm^2 after addition of the inhibitors (oil of Nigella Sativa and Elettaria Cardamomum respectively). The charge transfer resistance increases 383.6 ohm.cm^2 to 1871 ohm.cm2 and to 996 ohm.cm^2 in the electrochemical impedance spectrum after addition of oil of Nigella Sativa and Elettaria Cardamomum respectively. These inhibitors have been used in this study to show a high efficiency in the inhibition of corrosion of copper-zinc alloy in acid solution (HCl) and arrived at the 72.5 - 80% for both the oil of Nigella Sativa and Elettaria Cardamomum, whereas some of these molecules adsorbed on the surface of the metal is attributed to the formation of a film on the surface of the brass.

Keywords: Nigella Sativa oil, Elettaria Cardamomum oil, seeds, corrosion inhibition, electrochemical, Brass, hydrochloric acid.

INTRODUCTION

Using inhibitors is one of the most practical methods for protecting metals against corrosion, especially in acidic media [1-7]. This study was made due to the nature of the toxicity and the high cost of some compounds used as inhibitors, it became necessary to find and develop new materials to be used as inhibitors non-toxic and less expensive natural products can be considered as a good source for this purpose.

This research is one of the recent studies, because of expensive costs of corrosion which shows the world statistics that approximately 5% of the GDP, due to preventive measures to reduce the corrosion such as pipes buried and dyes Electroplating cathode protection anticorrosion countering that measures and preventive to reduce corrosion. The cost of operation and maintenance, and the things that have made corrosion interesting to study low or lack of quality of the product following outputs of contamination to corrosion, as the products of corrosion leading to change the chemical nature of the center of contamination often not desirable, because the business requirements require access to the clean and free product of contaminants with known specifications.

Thus, the appearance of corrosion in boxes contains food and simple of lead contamination and hence the loss of nutritional value, as well as the protection of the facilities and we have chosen as a model for the study of the copper alloy - zinc as they enter many household and operational and component tools grape in the industry of the financial of metal.

The selection of the inhibitors is not only based on their inhibition efficiency but also their environmental impact. Artificial and heterocyclic chemicals are not suitable for the corrosion inhibition process, in spite of their high efficiency, due to their hazardous impact on the environment [8]. Natural compounds and green inhibitors are the most suitable concerning their safe impact towards the environment. The pure plants extracts had efficient performance in preventing the corrosion of different metal in acidic media [9-13]. Green inhibitors like natural products from plant extracts and substances from other renewable sources are of interest to researchers who are interested in “green chemistry” or “eco-friendly” technologies [14-17].

The aim of our study is to investigate the influence of both Oil of Nigella Sativa and Elettaria Cardamomum on the corrosion of brass in HCl acid medium by electrochemical measurements: polarization curve and electrochemical impedance spectroscopy.

MATERIALS AND METHODS

2.1. Inhibitors

2.1.1. Plant material

Nigella Sative is an annual herbaceous plant pinnate leaves, divided into narrow lobes are lanceolate to linear and nectar tabs, the lower leaves are small and petal-like and are long. The flowers are small whitish upper petals and sepals petal-like and have many stamens inserted on the receptacle. The plant is hermaphrodite autonomous reproduction whose fruit is a capsule consisting of 3 to 6 carpels welded together to base persistent styles. Each capsule contains several triangular seeds and mature, they open and exposing the seeds to air makes the black, its ovoid 2 to 3.5 mm have 3-4 angles (**Figure 1**).

Figure 1. Plant and seeds of Nigella Sative

Figure 2. Plant and seeds of Elettaria cardamomum

Elettaria cardamomum is an herbaceous of the family Zingiberaceae. They belong to the order of Scitaminales, angiosperms monocots class. The cardamom native rainforests of Asia is now cultivated in Sri Lanka, Costa Rica, Vietnam and Guatemala, one of the largest exporters Current. This perennial, herbaceous about 1.5 meters tall, grows an average altitude (750 to 1500m) in tropical rainforest. Only after 3-4 years the plant. Beginning to bear fruit. These capsules of slightly elongated shape, pale yellow green to contain small black seeds. These fruits must be picked before maturity to keep the seed within the carpels (**Figure 2**).

2.1.2. Hydrodistillation apparatus and procedure

The extraction of essential oils of two plants studied is performed by hydrdistillation, installation is presented in **Figure 3**. The essential oil is lighter than water, it remains on the surface. There is thus obtained two immiscible phase that can be separated by settling: the essential oils and aromatic waters (or hydrosols) are loaded parts distilled water soluble species.

Placed grains and distilled water in the ball, it circulates cold water in the water cooler, then, with the heating mantle, bring to a boil. At the end of the hydrodistillation, is placed the entire distillate collected in a separatory funnel and allowed to rest. After settling, recovering the organic phase containing essential oils, and to remove any trace of water in essential oils, anhydrous sodium sulfate is added.

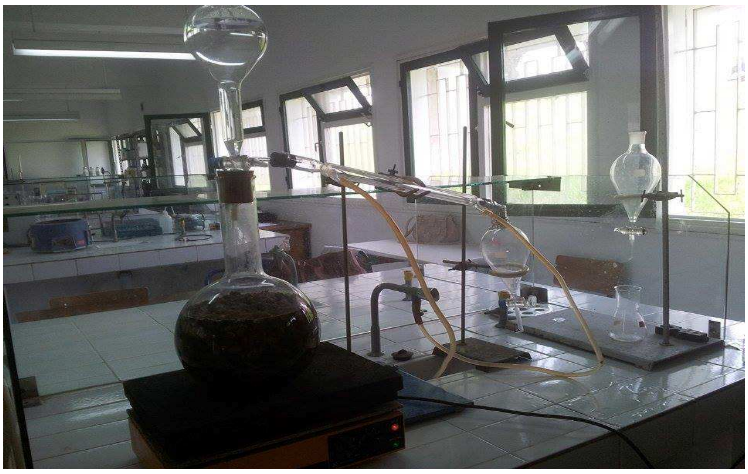


Figure 3. Technical of hydrodistillation

2.2. Solutions and mild steel samples preparation

The 1M solution of HCl was prepared by dilution of quality analysis Merck HCl 37% with distilled water. The test solutions were freshly prepared before each experiment by adding essential oil of *Nigella Sativa* and *Elettaria Cardamomum* directly to the corrosive solution. Experiments were conducted on several occasions to ensure reproducibility. Concentrations of essential oils were 0.25, 0.5, 1 and 1.5 g/ L.

2.3. Electrochemical measurements

As mentioned in the previous application notes, most corrosion phenomena are of electrochemical nature and consist of reactions on the surface of the corroding metal. Therefore electrochemical tests methods can be used to characterize corrosion mechanisms and predict corrosion rates.

2.3.1. Potentiodynamic polarization

This potentiostat was connected to a conventional three-electrode cell assembly. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes respectively. The working electrode is in the form of a rectangular disk from Brass of the surface 0.32 cm^2. These electrodes are connected to Voltalab PGZ 100 piloted by ordinate associated to ‘‘Volta Master 4’’ software. The scan rate was 1 mV/s started from an initial potential of -800 to -200mV/SCE. All experiments were repeated three times at the desired temperature of ±1 _C. Corrosion current densities were obtained from the polarization curves by linear extrapolation of the Tafel curves. Prior to the electrochemical measurement, a stabilization period of 30 minutes was allowed, which was proved to be sufficient to attain a stable value of corrosion potential (Ecorr).

Tafel polarization curves were plotted at a polarization scan rate of 0.5 mV/s. Anodic and cathodic curve slopes were extrapolated to corrosion potential, for the determination of the corrosion current densities (Icorr). The Tafel equations predict a straight line for the variation of the logarithm of current density with potential. Therefore, currents are often shown in semi logarithmic plots known as Tafel plots. This type of analysis is referred to as Tafel Slope Analysis. The Tafel slope analysis tool provides a quick estimation of the corrosion rate and the polarization resistance. The corrosion rate is calculated from the estimated corrosion current, Icorr, obtained from the intercept of the two linear segment of the Tafel slope.

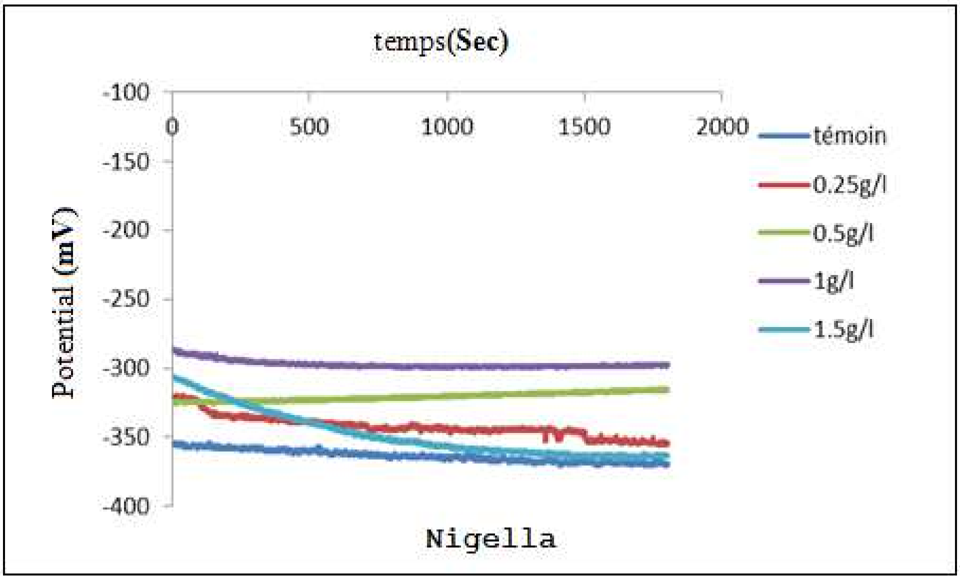
2.3.2. Electrochemical impedance spectroscopy
Electrochemical Impedance Spectroscopy (EIS) has many advantages in comparison with other electrochemical techniques. During EIS experiments, a small amplitude ac signal is applied to the system being studied. Therefore, it is a non-destructive method for the evaluation of a wide range of materials, including coatings, anodized films and corrosion inhibitors. It can also provide detailed information of the systems under examination; parameters such as corrosion rate, electrochemical mechanisms and reaction kinetics, detection of localized corrosion, can all be determined from these data. Electrochemical impedance spectroscopy (EIS) was carried out with the same equipment used for the polarization measurements, leaving the frequency response analyzer out of consideration.

Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mV/s. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz was superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potential after 30 min of exposure. All potentials were reported versus saturated calomel electrode (SCE).

The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility. All electrochemical studies were carried out with immersion time of 1 hour, with different inhibitory concentrations of *Nigella Sativa* and *Elettaria Cardamomum* essential oil, at 298 K.

RESULTS AND DISCUSSION

3.1. Potential measurements (OCP) in function of time
In the experimental part, special attention was taken in the stability of the potential abondon 30 min before each cycle of polarization and impedance. **Figure 4** shows the variation of the open circuit potential of the brass electrode over time in a 1M HCl solution in the absence and presence of various concentrations of essential oil of inhibitors studied to 298 K. It is apparent from **Figure 4** that the addition of inhibitors studied the potential HCl solution moves to abondon toward more positive values that implies that the addition of these oils causes ennoblement potential to abondon following formation a protective.



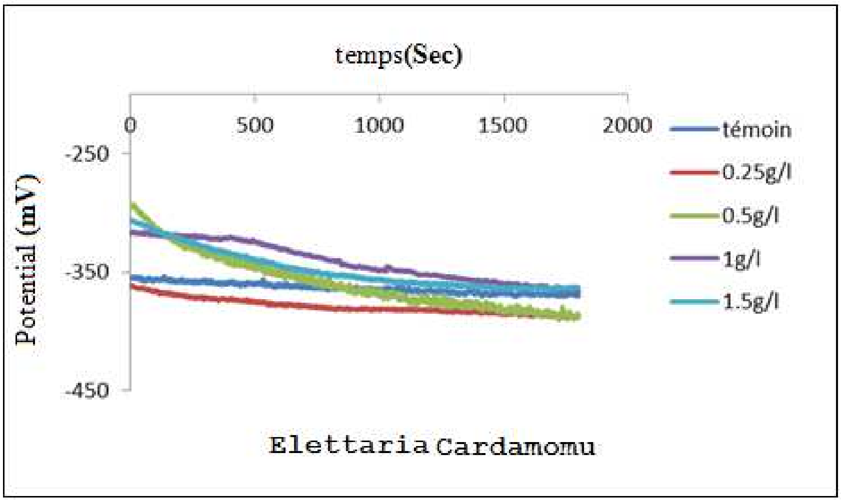


Figure 4. Potential change to the abandonment versus time brass in HCl 1M, with and without different essential oil concentrations studied at 298 K

3.2. Tafel polarization curves

In order to investigate whether corrosion products formed on the sample surfaces, the anodic polarization tests were carried out on the same surface and in the same test solution. All tests were done at room temperature using electrolytes that were not de-aerated during testing. Polarization curves for mild steel in presence and absence of different concentrations of essential oil of *Nigella Sative* and *Elettaria Cardmomum* in non-aerated solutions are shown in **Figure 5** & **6**. The extrapolation of Tafel straight line allowed the calculation of the corrosion current density (Icorr). The values of Icorr, the corrosion potential (Ecorr), cathodic Tafel slope (βc), and inhibition efficiency (E %) are given in **Table 1** and **2** for essential oil *Nigella Sative* and *Elettaria Cardmomum* respectively. The (E %) was calculated using the following equation [11-18]:

$$E(\%) = \frac{I°corr - Icorr}{I°corr} x100 \quad \textbf{(1)}$$

Where $I°_{corr}$ and I_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential.

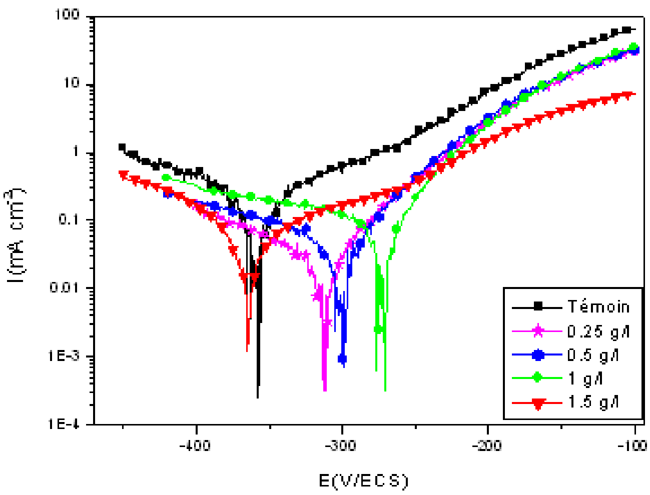


Figure 5. Tafel polarization curves in HCL 1M with and without *Nigella Sative* oil at different concentrations at 298 K

A first analysis of these curves shows that the essential oil of ***Nigella Sative*** has an effect on the anodic and cathodic branches Taffel implying that this inhibitor affects both the H reduction reaction + H_2 that the corrosion reaction of brass. The black cumin oil is a mixed inhibitor. The reduction of the proton:

$$\mathbf{2H^+ + 2e- \leftrightarrow H_2}$$

A reaction requiring two successive steps.

The first is the reaction proper discharge (or reaction Volmer):

$$\mathbf{H^+_{ads} + e^- \text{ ------------- > } H_{ads}}$$

The opinion, however, differs on the second step could be:

- either purely chemical:

$$\mathbf{H_{ads} + H_{ads} \text{ ---------------- > } H_2} \qquad \text{(Réaction de Taffel)}$$

- Either electrochemical either:

$$\mathbf{H_{ads} + H^+ + e^- \text{ ------------ > } H_2} \qquad \text{(Réaction d'Heyrovski)}$$

In our case, the cathode curves show a linear portion (straight Tafel) indicating that the reduction reaction of hydrogen at the brass surface is in a pure activation mechanism. **Table 1** summarizes the values of electrochemical parameters determined from polarization curves: The density of corro-sion current (I corr), the corrosion potential (E corr), cathodic Tafel slope (bc) and the effectiveness corrosion inhibiting E (%).

Table 1. Electrochemical parameters and inhibitory efficacy of brass corrosion in HCl 1M without and with addition of different concentrations of Nigella Sative oil

Concentration (g/l)	E_{corr} (mV)	i_{corr} (mA/cm^2)	-bc (mV/dec)	E (%)
Témoin	-357,42	0,204	117	----
0,25	-311,57	0,140	221	31,4
0,5	-301,80	0,103	172	49,5
1	-273,34	0,076	83	62,7
1,5	-363,85	0,042	119	79,4

Examination of the results of the **table1**, shows that: increasing the concentration of inhibitor which reduces Icorr reaches 0.042 mA/cm^2 to 1.5g / l corresponding to an inhibitory efficiency of 79.4%. However, the corrosion potential is moved very slightly toward the anode values.

The addition of the inhibitor changes slightly cathodic slope Taffel bc, showing that the brass surface is changed when the *Nigelle* oil is added to the aggressive environment.

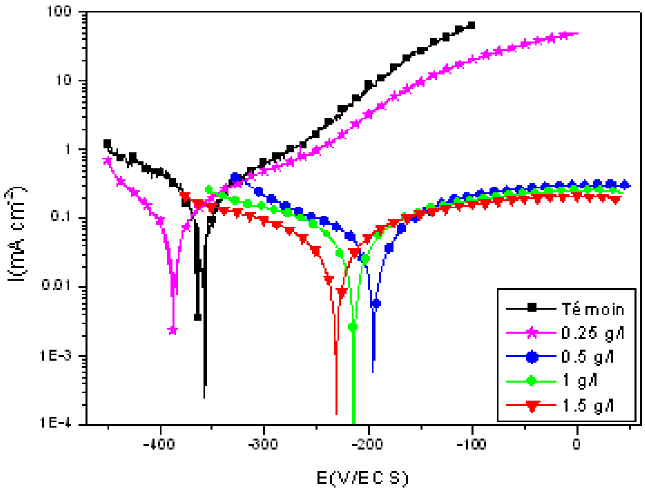


Figure 6. Tafel polarization curves in HCL 1M with and without Elittaria Cardamomum oil at different concentrations at 298 K

The comparative study of these curves allows us to make the following findings:
→The cathodic and anodic branches are slightly affected by the presence of this inhibitor.
→The addition of cardamomum essential oil is accompanied by a net decrease of the anodic and cathodic current density as the concentration of inhibitor increases.
→The values for Ecorr corrosion potentials move in the anodic direction with increasing compound concentration.

All these findings support the conclusion that the oil of cardamomum is a mixed inhibitor. The anodic branches Taffel are lines indicating a H$^+$ reduction mechanism under activation control.

The anodic and cathodic curves exhibit a wide range of linearity indicating that the law of Taffel is checked in the anode and cathode area. Discharging the proton is then effected by a pure kinetic activation.

The electrochemical parameters obtained following the operation of these lines of Taffel are given in **Table 2**.

Table 2. The electrochemical parameters deduced from curves Tafel

Concentration **(g/l)**	E_{corr} **(mV)**	i_{corr} **(mA/cm^2)**	-bc **(mV/dec)**	E **(%)**
Témoin	-357,42	0,204	117,4	----
0,25	-386.76	0,143	221,3	29.9
0,5	-194 .47	0,123	172,0	39.7
1	-213.31	0,106	83,2	47.5
1,5	-230.05	0,056	119,0	72.5

From **Table 2**, we see that at low concentration has the effect of moving Ecorr in the direction of cathode potential of the inhibitor and to the anodic direction to another concentration.

I_{corr} decreases as the concentration of inhibitor increases .This implies an increase of the inhibitory efficacy which reaches a value of 72.5% to 1.5g / l of the inhibitor.

3.3. Electrochemical impedance measurements

Among the different electrochemical techniques that can be used to study corrosion inhibitors, EIS appears as powerful tool for the information that can provide, as for example, double layer capacitance, C_{dl}, and polarization resistance, Rp, values. Changes in these parameters as a function of time or with respect to other variables, allow obtaining important information about the kinetics of the corrosion process being involved [19, 25]. In some cases impedance data obtained at the corrosion potential, Ecorr have the shape of depressed semicircles with the centre of the semicircle below the real axis. The corrosion behaviour of mild steel in 1M HCl solution, in the absence and presence of *Nigella Sative* and *Elettaria Cardamomum* oil, was investigated by the EIS at 308 K after 1 hour of immersion. The charge-transfer resistance values were obtained from the diameter of the semicircles of the Nyquist diagrams. The inhibition efficiency (E %) of the inhibitor has been found out from the charge transfer resistance values using the following equation:

$$E\,(\%) = \left(1 - \frac{Rt}{R't}\right) * 100 \qquad (2)$$

where, R’t and Rt are the charge transfer resistance in absence and in presence of inhibitors, respectively.

All electrochemical measurements were done in unstirred and non-aerated solutions. The electrochemical impedance plots for mild steel in 1M HCl solution in the absence and presence of various concentrations of inhibitors studied are shown in **Figure 7** & **8**. **Table 3** & **4** summarizes impedance data from the EIS experiments carried out both in the absence and presence of increasing essential oil and extract concentrations.

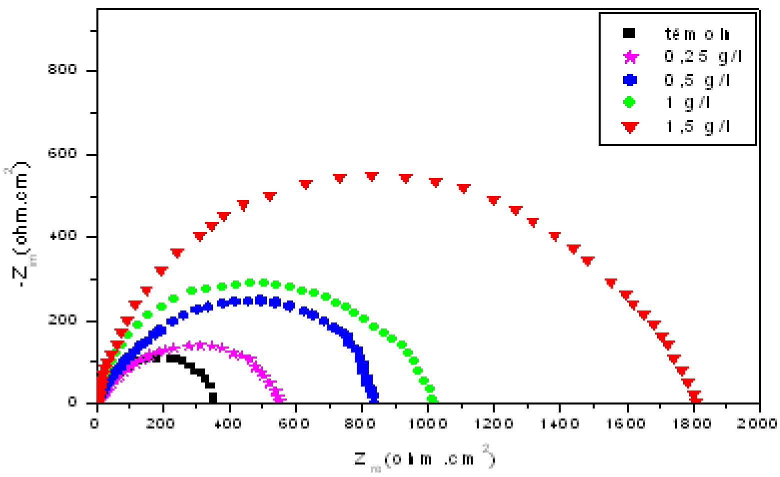


Figure 7. Nyquist plots in absence and presence of different concentrations of *Nigella Sative* oil in 1M HCl

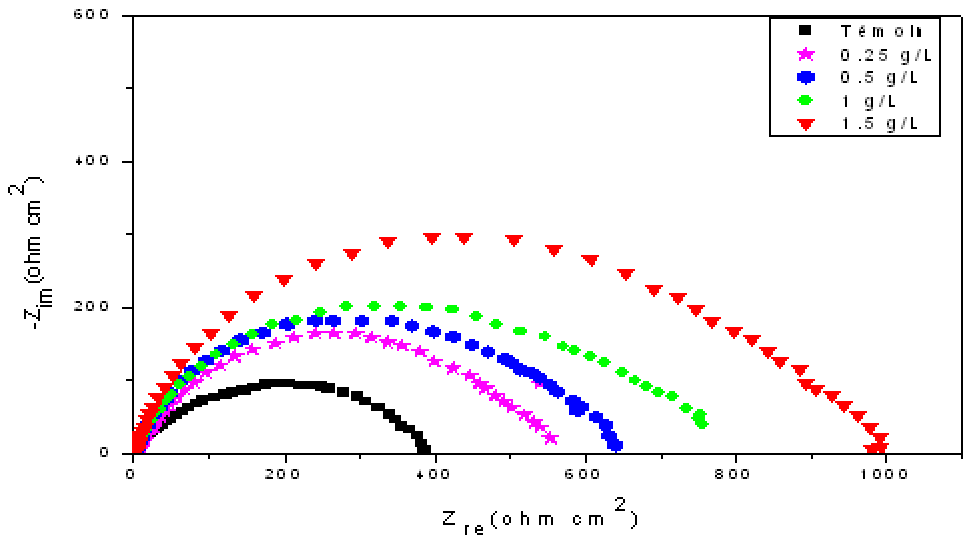


Figure 8. Nyquist plots in absence and presence of different concentrations of *Elettaria Cardamomum* oil in 1M HCl

We note that for all concentrations, there is the presence of a single capacitive loop. The latter corresponds to the charge transfer resistance. We also note that adding oil of *Nigella Sativa* and *Elittaria Cardamomum* does not affect the nature of the loops which implies that the corrosion mechanism is not changed by the addition of inhibitors.

From these diagrams made in corrosion potential we were able to access the values of R_t charge transfer resistance and therefore to the inhibitory efficacy of the studied inhibitors under the operating conditions used.

The set of measurements of impedance parameters from these Nyquist plots are pooled in **Tables 3** and **4**.

Table 3. Electrochemical impedance parameters in the absence and presence of the inhibitor at different concentrations of the essential oil Nigella Sative

Concentration **(g/l)**	Rt **(ohm.cm^2)**	Cd **(µF/cm^2)**	E **(%)**
Témoin	383,6	331,8	----
0,25	536,5	293,2	28,5
0,5	816,9	194	53 ,0
1	961,3	52,31	60,1
1,5	1871,0	42,51	80

Table 4. Electrochemical impedance parameters in the absence and presence of the inhibitor at different concentrations of essential oil of Elettaria Cardmomum

Concentration **(g/l)**	Rt **(ohm.cm^2)**	Cd **(µF/cm^2)**	E **(%)**
Témoin	383	332	---
0.25	553	320	30.74
0.5	639	314	40.06
1	761	287	49.67
1.5	996	127	61.54

From **Tables 3** & **4**, we can make the following findings:

The inhibitory effectiveness increases with the concentration of the inhibitor to reach a maximum value of 80% and 61.54% at 1.5 g / L in the presence of oil of *Nigella Sativa* and *Elettaria cardamomum* respectively.

Increasing the concentration of the inhibitor was accompanied by an increase in R_t values and a decrease in C_{dl} values. C_{dl} is decreased due to adsorption of the inhibitor to the brass surface which has the effect of reducing the active surface of the electrode.

This decrease is accompanied by an increase of the effectiveness of inhibition.

CONCLUSION

From the overall experimental results and discussion the following conclusions can be deduced:

- Tafel polarization measurements show that essential oil of Nigella Sative and Elettaria Cardamomum act essentially as a mixed type inhibitor.
- The increase in the charge transfer resistance and double layer capacitance values, with the increase in the inhibitor concentration, showed that essential oil of Nigella Sative and Elettaria Cardamomum formed protective layers on the mild steel surface, covering areas where HCl solution degrades and corrodes slowly.
- Inhibition efficiency increases with increase in the concentration of the essential oil of Nigella Sative and Elettaria Cardamomum.
- The corrosion process was inhibited by adsorption of the organic matter on the mild steel surface, obtaining the formation of the film on the metal/acid solution interface, decreasing the degradation of the material.
- Results obtained through electrochemical tests demonstrated that the essential oil of Nigella Sative acts as efficient corrosion inhibitor of the mild steel in 1 M HCl solution, better than essential oil of Elettaria Cardamomum.

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