# Corrosion inhibition of lead in 0.1 M Na_2CO_3 solution by the essential oil of green mint (*Mentha viridis*)

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Abstract

The anticorrosive effect of the essential oil extracted from an aromatic and curative plant, *mentha viridis*, on lead in 0.1M Na_2CO_3 medium, was studied by the methods of potentiodynamique polarization, chrono-amperometry and spectroscopy impedance. The effect of temperature was determined with and without the inhibitor oil in the range of 5 to 35°C. The essential oil of green mint has an anticorrosive effect which reached 80 % at the concentration of 2000 ppm. The study of potentiodynamic polarization showed that this oil corresponds to an inhibitor of mixed type with an anodic predominance. The green mint oil adsorption is made according to the model of Langmuir.

Keywords: Lead; corrosion; inhibition; essential oil; *mentha viridis*; adsorption
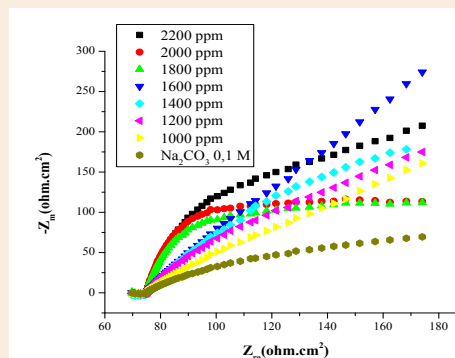
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Introduction

Corrosion is the deterioration of a metal by an attack or a chemical reaction with its environment. It is an uninterrupted and constant problem, and is often difficult to eliminate completely. Corrosion affects most industrial sectors and can cost thousands million dollars every year [1]. The lead is a metal widely used in industry, its main use in the world is in manufacturing of lead accumulator batteries. These last are used in the automotive sector, that of urgent devices (hospitals), and that of industrial products (computers, wagons and forklifts) [2]. A car battery contains about 10 kg of lead [3].The corrosive medium degrades the material and the performances of batteries are affected[4].

Lead is also used as stabilizer in plastic pipes, decorative glass and coatings of roofing, and it enters the composition of consumption products such as pigments and coatings (artists' supplies).The problems of corrosion in industry and manufacture of accumulators in general were solved thanks to the selection of the appropriate materials and / or by changing medium to make it less aggressive [5]. Solutions (acid or base) are widely used in industry. Pickling, industrial cleaning and scaling are the important areas where these solutions are the most applied [6].

It is then necessary to apply the mode of protection adapted to the conditions of medium. From this point of view, the struggle against corrosion can be envisaged in three ways: an organic or metallic coating, an organic protection, and an inhibition of chemical type or a green inhibition [7]. This last mode of protection which is the most preferred in several cases is the objective of this study [8, 9, 10, 11].

In accordance with the definition given by the National Association of Corrosion Engineers (NACE)"*an inhibitor is a substance which postpones corrosion when it's added to an environment in weak concentration*" [12].Generally the inhibitors of corrosion act by adsorption on the surface of the metal. The adsorption of inhibitors is influenced by

nature and superficial load of the metal, by the type of aggressive electrolyte and by the chemical structure of inhibitors. There are two main types of correlations between the adsorbed inhibitor and the metallic surface which are; the physisorption and the chimisorption. The most commonly used inhibitors are chemical, toxic for man and environment.

The aim of this work is to study the inhibitory activity of the essential oil of *Mentha viridis* against corrosion of lead in 0.1M Na_2CO_3 medium by the methods of electrochemical polarization, chrono-amperometry and spectroscopy electrochemical impedance. The effect of temperature was also studied.

Experimental

Extraction of the essential oil of *Mentha viridis*:

Fresh leaves of the green mint were harvested of the region of Elbrouj, Morocco, during months July and August of year 2013. The essential oil of the mint was obtained by hydro distillation from fresh leaves with the Clevenger apparatus during 3 h on average. The essential oil was recovered in an opaque bottle and stocked at 4°C.

A portion of the oil was used for the analysis of the chemical composition by gas chromatography, and the other part was used for the tests of the anti-corrosion activity.

Preparation of the solution

The solution of 0.1 M sodium bicarbonate (Sigma-Aldrich) was prepared with distilled water. Test solutions were freshly prepared before each experiment by adding the oil directly to the etching solution. Experiments were repeated tree times to verify reproducibility.

Electrochemical measurements

The electrochemical experiments were performed in a pyrex cell, equipped with a conventional three-electrode assembly: working electrode lead as cup-shaped disc with a geometric area of 1 cm^2, platinum as a counter electrode and the electrode SCE as saturated calomel reference electrode. The lead disc was abraded with sandpaper to increase particle size up to 1200, degreased with acetone, rinsed with distilled water and dried before each test. The measurements are performed with an assembly comprising a potentiostat-galvanostat PGZ100, and a radiometer type coupled with "voltamaster4" software.

The current-potential curves are obtained by potentiodynamic method; the potential applied to the sample varies continuously with a scanning rate of 2 mV/s between 1000 and -1000mV. Chrono- amperometric curves were plotted at a potential of 150 mV for 3600 seconds.

The measures of electrochemical impedance spectroscopy (EIS) were performed with the same electrochemical system. The frequencies between 100 kHz and 10 Hz were superposed on the corrosion potential. The diagrams given in the impedances are Nyquist representation.

Results and Discussion

Analysis of the chemical composition of the oil

The average yield of the essential oil extracted from the fresh leaves of *Mentha viridis* is in the range of 0.4%.
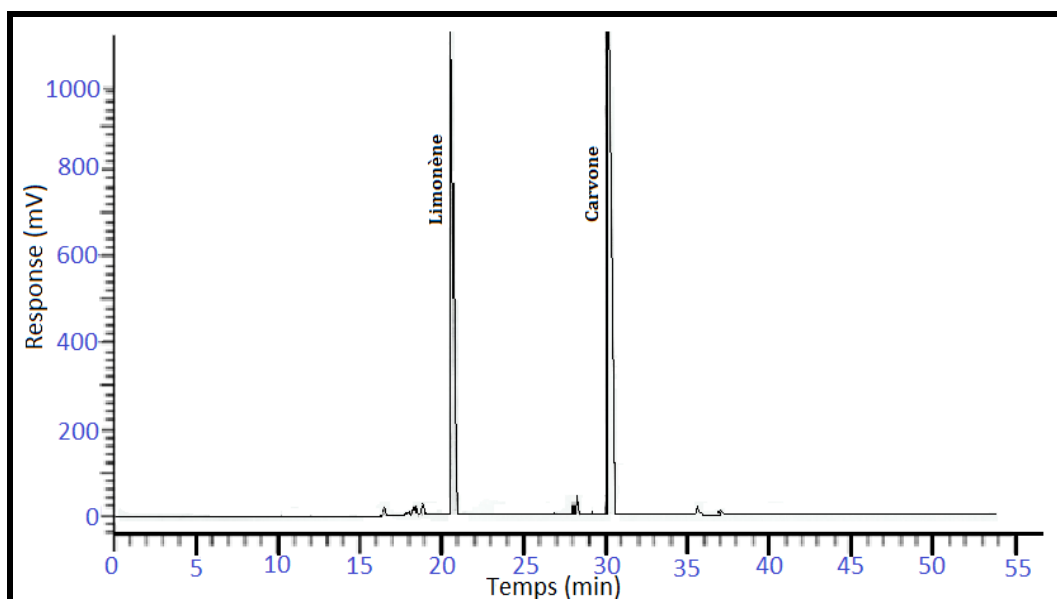
Figure 1 Chromatogram of the essential oil of *Mentha viridis*

Table 1 Chemical components of the essential oil of *Mentha viridis*

Peak	Time (min)	Area %	Component
1	16.197	0.32	α-pinène
2	18.289	0.35	β-pinène
3	18.717	0.44	Myrcène
4	20.737	29.64	Limonène
5	28.021	0.83	α-terpinéol
6	30.164	68.43	Carvone

Electrochemical study of lead in a Na2CO3 solution 0.1 M :

Figure 2 shows polarization curve of lead in a 0.1 M sodium bicarbonate solution at 25 ° C.
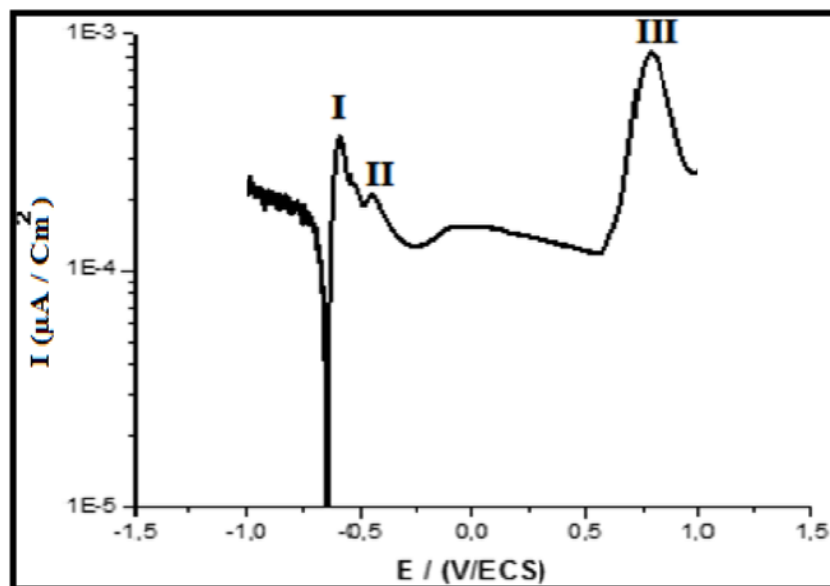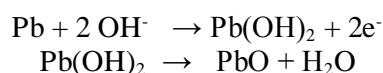

Figure 2 Lead polarization curves in 0.1 M Na_2CO_3 at 25°C

The anodic portion of the curve contains three peaks (I, II, and III), the first peak I is located at -0,582 V / SCE, which is due to the formation of $Pb(OH)_2$ or PbO by the following reactions [13]:

$$Pb + 2\ OH^- \rightarrow Pb(OH)_2 + 2e^-$$
$$Pb(OH)_2 \rightarrow PbO + H_2O$$

The second anodic peak is located at -0.45 V/SCE corresponding to the training $Pb(OH)_4$ or PbO_2 by the following reactions [14]:

$$PbO + H_2O + 2OH^- \rightarrow Pb(OH)_4 + 2e^-$$
$$Pb(OH)_4 \rightarrow PbO_2 + 2\ H_2O$$
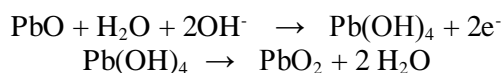
The thermodynamically unstable dehydration of $Pb(OH)_4$ results in the formation of PbO_2, which is responsible for the formation of a passive film, making the coated surface, and the anodic current density falls to a lower value (I_{pass}) indicating passivation [15].

The third peak (III) is observed at about 0.789 V/ECS beyond the plateau of passivity; it cannot be particularly assigned to any anodic oxidation reaction. Several authors attributed this observation to the region of transpassivity, which is generally due to release of oxygen which occurs most likely on acid film H_2PbO_3 [16].

For higher anodic potentials, the field of transpassivity is achieved due to the oxidation of the solvent according to the following reaction:

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$$
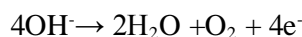
Effect of concentration:

Measurement of polarization:

Fig. 3 shows the effect of the concentration of green mint oil on the cathodic and anodic behavior of lead in a solution of 0.1 M Na_2CO_3, which was studied by measurements of polarization. Table 2 shows the parameters of electrochemical lead, determined from measurements of polarization, such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), passivation current density (I_{pass}) and efficacy of inhibition E (%) calculated by Equation 1:

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

Where I'_{corr} and I_{corr}: are respectively the current densities with and without addition of inhibitor.

It is clear from Figure 3 that the anodic dissolution of the metal was inhibited with the addition of mint oil in the corrosive solution.

In the experimental conditions of this test, the cathodic branch represents the reaction of hydrogen clearing and the anodic branch represents the dissolution of lead. The examination of these results reveals that the density of corrosion (Icorr) decreased in the presence of the inhibitor. This behavior reflects the ability of the essential oil of green mint to inhibit corrosion of lead in a solution of 0.1 M Na_2CO_3.
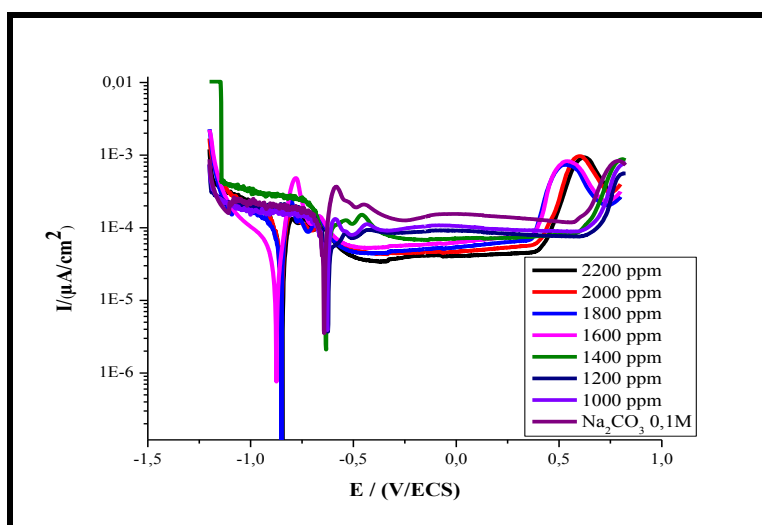

Figure 3 Lead polarization curves in a 0.1 M Na_2CO_3 solution with and without inhibitor at 25°C

According to recorded results in fig. 3 and table 2, the percentage of the green mint essential oil inhibitive effect increases depending on its concentration. This suggests that increasing the concentration of inhibitor increases the number of adsorbed molecules on the lead surface, blocking the active sites and protect the metal. The inhibitive effect of this oil reached its maximum value of 80.29 % for a concentration of 2000 ppm. From table 2, the passivation current increase from $1.5366.10^{-4} \mu A/cm^2$ to $3.9685.10^{-5} \mu A/cm^2$, this decrease is mainly due to the adsorption of oil on metal surface.

On the other hand, it is necessary to note that the addition of this inhibitor causes a slight shift of the corrosion potential towards cathodic and anodic values, which highlights the mixed nature of mint with anodic dominance. [16-17].

Table 2 Parameters derived electrochemical Tafel free lead in 0.1 M Na_2CO_3 with and without inhibitor at 25°C

Concentration in ppm	I_{corr} (µA / Cm^2)	E_{corr} (mV / ECS)	I_{pass} (µA / Cm^2)	Ep %
0	28.4762	-644.5	$1.5366.10^{-4}$	--------
1000	27.9007	-636.8	$7.1875.10^{-5}$	20.17
1200	18.8164	-653.1	$6.0803.10^{-5}$	33.92
1400	11.7087	-643.6	$5.1830.10^{-5}$	58.88
1600	7.7488	-677.2	$4.7008.10^{-5}$	72.78
1800	5.6967	-641.3	$4.0580.10^{-5}$	79.99
2000	5.6696	-639.5	$3.9685.10^{-5}$	80.09
2200	5.6630	-632.3	$3.0217.10^{-5}$	80.11

Chrono-amperometry:

Experiences of time-current chrono-amperometric were conducted to identify the type of lead corrosion in a solution of sodium bicarbonate in the absence and presence of inhibitor. The chrono-amperometric curves measured at 150 mV of lead 0.1M Na_2CO_3 medium without and with addition of 2000 ppm of mint essential oil are showed in Figure 4.

Figure 4 shows that the oxidation currentdecreases apace without inhibitor, 500 min after it becomes stable, andthe current is constant in presence of the inhibitor.Itisclear thattheleadina Na_2CO_3 solutionalone records higher oxidation currentvalues due to leaddissolutionbycorrosive attackof OH-ions.

The initial increase in currentoccursbecause the lead dissolves in a first time to form thePb$(OH)_4$which isunstable and is transformed into PbO_2 where the current decreases with time due to the formationof an oxidelayer (PbO_2). The formationof sucha layer provides partial protection and does not allow the current to rise.
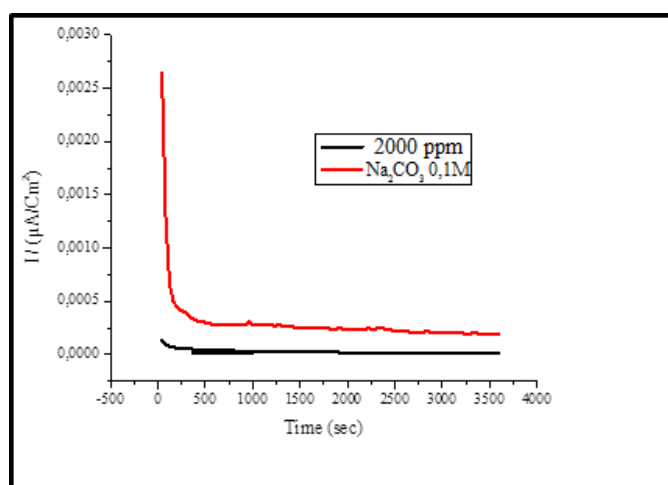

Figure 4 Chrono-amperometric curves at 150mV for lead in 0.1M Na_2CO_3solution with and without 2000 ppm mint oil at 25 °C

Adding 2000ppm of mint essential oil causes agreat decreaseincurrent values,which is probably due to molecule adsorption of the inhibitor on the lead surface,blocking the active sites and there by preventing its dissolution. These results are in good agreement with the polarization data,where Fig.3 and Table2,bothconfirm that the inhibitor has the ability to inhibit the corrosion of lead.

Electrochemical impedance spectroscopy:

Nyquist Impedance curves of lead in 0.1M Na_2CO_3in the absence and presence of different concentrations of mint oil are shown in Figure5.

The inhibition effect EEIS (%) was calculated using Equation 2:

$$E_{EIS}\% = \frac{R_T - R'_T}{R_T} \times 100 \quad (2)$$

Where R_T and R'_T are the charge transfer resistances with and without inhibitor respectively.Double layer capacity Cdl values were obtained at the maximum frequency (f_{max}), where the imaginary part of the Nyquist curve is maximum, and calculated using the equation 3:
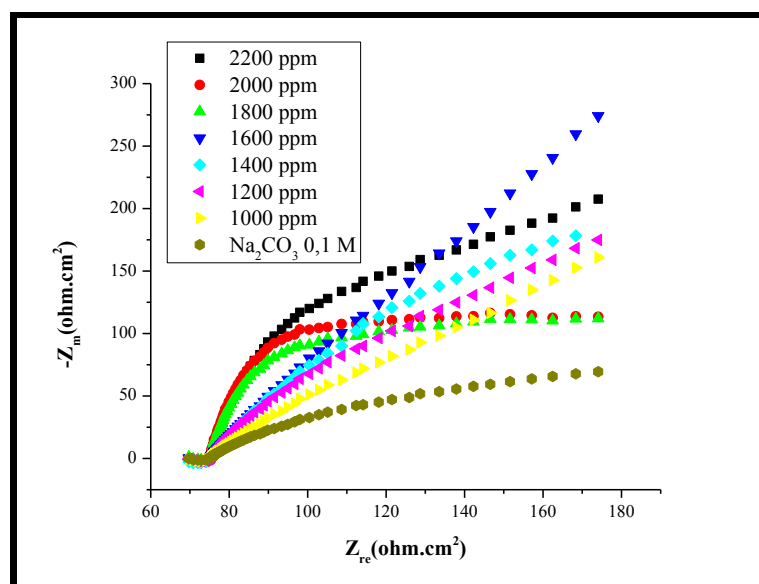
$$C_{dl} = \frac{1}{2.\pi.fmax.Rt} \quad (3)$$

Figure 5 Lead Nyquist curves in 0.1M Na_2CO_3at various concentrations of mint oil to 25 °C.

The impedance spectra are simple semicircleforms, and the semicircles diameter increases with increasing concentration of inhibitor. The presence of a single half-circle indicates that the charge transfer occurs at the electrode/solution interface, and the transfer process of the reaction of lead in the presence of corrosion inhibitor doesn't change its dissolution mechanism [18, 19]. The dielectric parameters are given in Table 3. Values R'_Tincreases with the increase of the concentration of green mint while C_{dl} values decrease. Higher values R'_Tmay suggest the formation of a protective layer onelectrode surface [20], which blocks its dissolution. These results are in good agreement with those of the polarization.

Table 3 Impedance parameters of lead in 0.1M Na_2CO_3 at different concentrations of mint oil at 25° C.

Concentration in ppm	R_s ($\Omega . Cm^2$)	R_t ($\Omega . Cm^2$)	C_{dl} ($\mu F / cm^2$)	E_{EIS} (%)
0	74.47	236.9	67.16	--------
1000	87.02	304.5	25.17	22.20
1200	71.56	344.0	17.75	31.15
1400	68.18	578.5	12.65	59.05
1600	61.72	936.3	9.03	74.70
1800	58.17	1072.6	7.25	77.91
2000	50.22	1189.8	7.04	80.08
2200	47.68	1217.9	6.85	80.55

From Table 3, it is found that the charge transfer resistance increases with the concentration of inhibitor, it reaches a value of 1254.1 Ω. Cm^2 at a concentration of 2000 ppm. In fact, the essential oil adsorbed onto the surface of the lead forming a conductive film. Similarly, it is noted that the value of C_{dl} decreases this results in a large decrease in the double layer of the metal-solution interface.

Effect of temperature:

Temperature corrosive environment is one of the factors affecting the inhibitory efficacy of a compound as well as the behavior of substrates in a given corrosive environment. For example an increase in temperature facilitates the dissolution of the organic compounds increases the diffusion rate and uniform surfaces, preventing the formation of separate anodic and cathodic areas.

Given the importance of this factor, we performed tests of polarization and impedance at different temperatures (5-35°C) in the absence and presence of 2000 ppm mint oil, in 0.1 M Na_2CO_3.

Measurement of polarization:

The effect of temperature on the lead without and with addition of mint oil,carried by the polarization measurements is respectively given in **Figure 6** and **7**. The electrochemical parameters derived from these figures are given in **Table 4**.

Figure 6 ,7 and **Table 4** indicate that there is a general increase in the corrosion intensity with increasing temperature from 5 to 35°C.The solution becomes more corrosive with the temperature rise and the corrosive power becomes less effective. This implies that this inhibitor is adsorbed on the metal by electrostatic bonds(weak bonds). This type of temperature-sensitive links cannot fight effectively against corrosion with increasing   temperature [21].
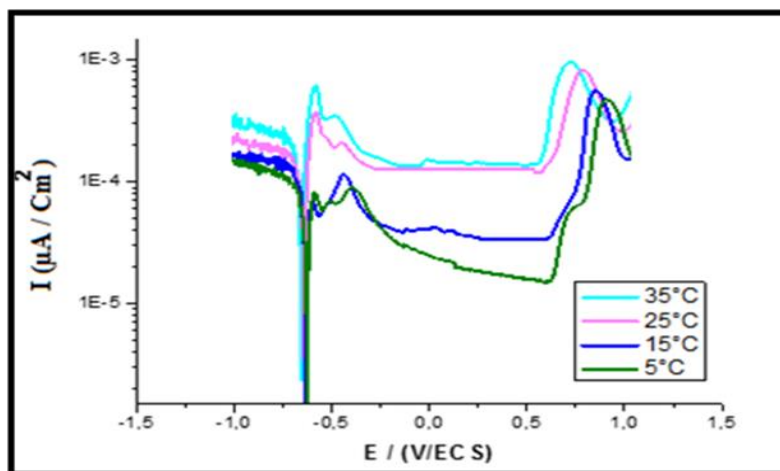
Figure 6 Lead polarization curves in a $0.1MNa_2CO_3$ solution without inhibitor at different temperatures.
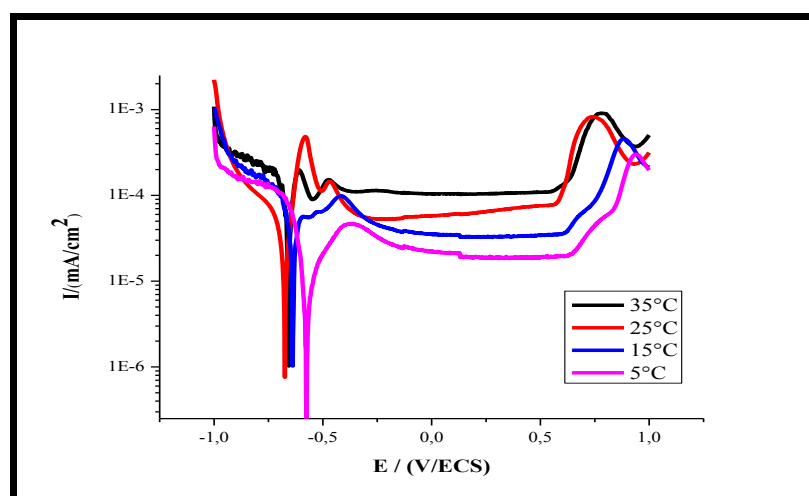

Figure 7 Lead polarization curves in a $0.1MNa_2CO_3$ solution with 2000ppm inhibitor at different temperatures.

Table 4 Lead electrochemical parameters in a $0.1MNa_2CO_3$ solution with and without 2000ppm mint oil at different temperatures.

Concentration in ppm	Temperature (K)	I_{corr} ($\mu A/cm^2$)	E_{corr} (mV/SCE)	I_{pass} ($\mu A/cm^2$)	Ep (%)
	278	16.2547	-631.2	$1.8884.10^{-5}$	---
	288	20.4262	-633.4	$3.5982.10^{-5}$	---
Blank	298	28.4762	-644.5	$1.5366.10^{-4}$	---
	308	35.3222	-658.5	$1.4138.10^{-4}$	---

	278	3.5690	-621.9	$1.9152.10^{-5}$	87.46
	288	5.2361	-640.6	$3.2723.10^{-5}$	81.61
2000 ppm	298	5.6967	-641.3	$4.0580.10^{-5}$	79.99
	308	9.5682	-650.7	$1.0429.10^{-4}$	66.39

Electrochemical impedance spectroscopy (EIS)

The effect of temperature on the behavior of the lead corrosion in 0.1M Na_2CO_3 containing an inhibitor concentration of 2000ppm is considered in the temperature range of 5-35°C using impedance diagrams (Fig.8and9), the corresponding results are summarized in Table 5.
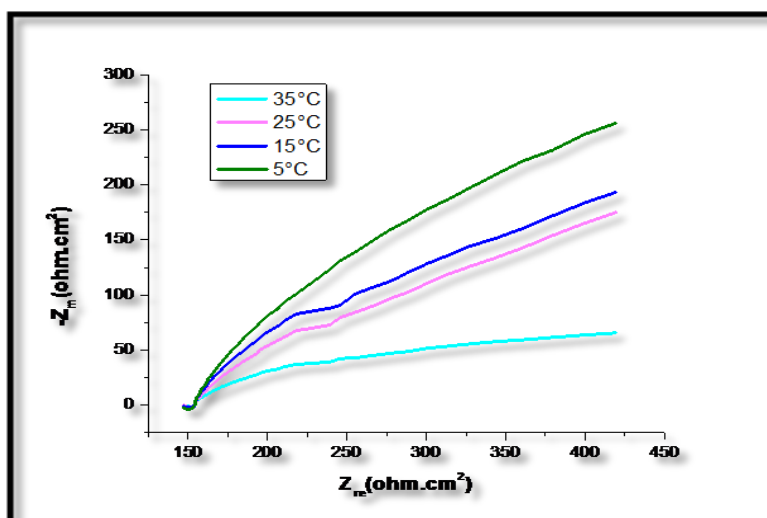

Figure 8 Lead Nyquist curves in 0.1 M Na_2CO_3 at different temperatures
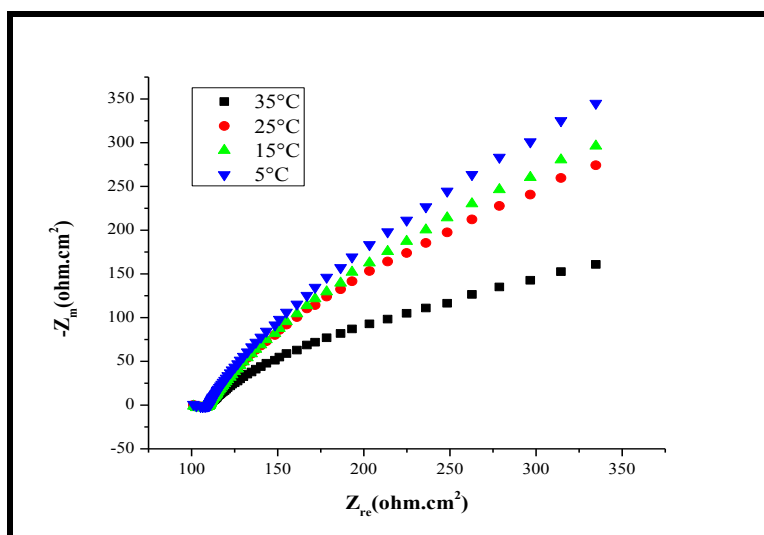

Figure 9 Lead Nyquist curves in0.1 M$Na_2CO_3$with 2000 ppm of mint oil at different temperatures

Table 5 Lead electrochemical parameters in 0.1 M Na_2CO_3 with and without 2000 ppm mint oil at different temperatures.

Concentration in ppm	Temperature (K)	R_s ($\Omega.\ Cm^2$)	R_t ($K\Omega.\ Cm^2$)	C_{dl} ($\mu F\ /\ cm^2$)	E_{EIS} (%)
Blank	278	107.1	1.337	11.90	---
	288	81.56	0.874	18.20	---
	298	74.47	0.236	67.16	---
	308	65.22	0.153	70.36	---
2000 ppm	278	109.4	13.423	4.19	90.04
	288	75.29	5.352	5.22	83.67
	298	58.17	1.185	7.25	80.09
	308	51.84	0.593	9.04	74.22

It is underlined that the inhibitor effect is influenced by the temperature; it decreases with increasing temperature, it is up to 5°C where it reaches 90%.

Determination of the activation energy:

In the case of corrosion in a basic medium, many authors [22-23] using the Arrhenius equation to account for the effect of temperature (T) on the rate of corrosion and therefore believe that the rate corrosion logarithm is a linear function of T^{-1}.

We can calculate the activation energy from the following equation (4):

$$Ln\ k = -\frac{E_a}{R.T} + A \quad (4)$$

Where Ea is the activation energy, T the absolute temperature, R is the gas constant, and A is the Arrhenius pre-exponential factor.

Changes in the logarithm of the corrosion rate as a function of T^{-1} (Fig. 10) provide lines indicating that the Arrhenius law is enforced.
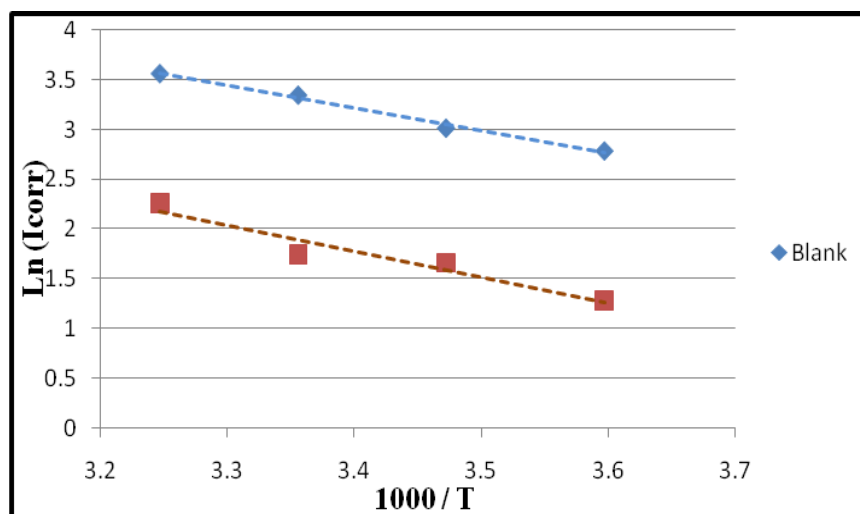
Figure 10 Lead curves Arrhenius plots in 0.1 M Na_2CO_3 in the absence and the presence of inhibitor

Table 6 The activation energy of lead with and without inhibitor

	Blank	**2000 ppm mintoil**
E_a (J / mol)	18.93	21.58

Table 6 shows that in the presence of an inhibitor the activation energy increases, so that IE% decreases as the temperature increases. This behavior could indicate that in the presence of an inhibitor the activation mechanism is assigned to physisorption on the lead surface [24-25].
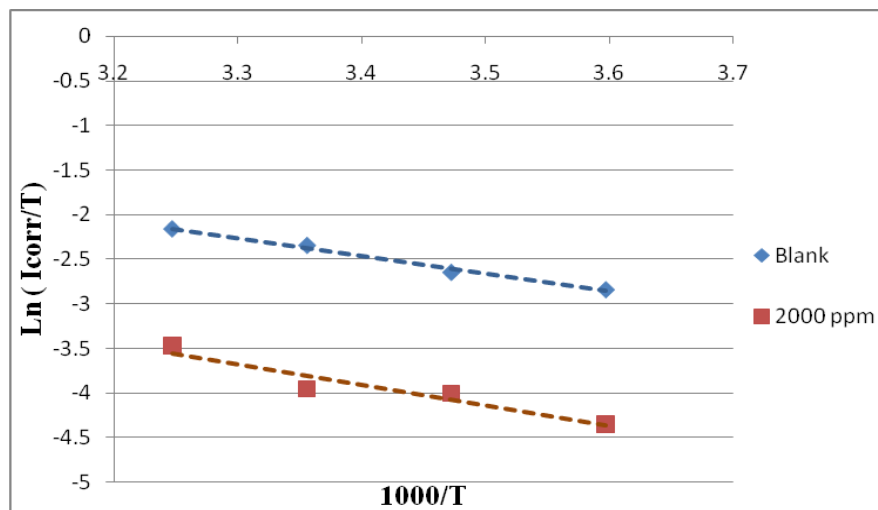

Figure 11 Relationship between Ln (I_{corr}/T) and1000/Tat different temperatures

The kinetic parameters, the enthalpy and entropy of the corrosion process are also estimated from the study of the effect of temperature. An alternative formulation of Arrhenius equation 5 is:

$$I_{corr} = \frac{RT}{Nh} \times \exp\left(\frac{\Delta S^*}{R}\right) \times \exp\left(-\frac{\Delta H^*}{RT}\right) \qquad (5)$$

Where h is Planck's constant, N is the Avogadro number, ΔS^* is the entropy of activation, ΔH^* is the activation enthalpy. Figure 11 shows plots of Ln (Icorr/T) compared to 1/T. straight lines are obtained with a spawning - $\Delta H^*/R$ is an intercept $\left(Ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^*}{R}\right)$, from which the values ΔS^* and ΔH^* can be calculated, these values are given in Table 7:

Table 7 The values of the activation parameters of lead inNa_2CO_3in the absence and presence of 2000 ppm of the green mint essential oil

Inhibitor	ΔH^* (J/mol)	ΔS^*(J/mol.K)
Blank	16.50	-161.92
2000 ppm	19.15	-164.88

The thermodynamic data (ΔS^* and ΔH^*) for the reaction of lead dissolution in a$0.1MNa_2CO_3$ solution is higher in the presence of the inhibitor than in its absence. The positive sign of ΔH^* reflects the endothermic nature of the process of lead dissolution, which suggests that the slow dissolution of the lead is in the presence of inhibitor [26]. By comparing the values of the activation data ΔS^* entropy inTable7,it is clear that the activation entropy decreases more negatively to a great extent in the presence of inhibitor than in its absence, which reflects the formation of a stable layer controlled by the inhibitor on the lead surface [27].

The value of the enthalpy of the free energy ΔG^* is derived by the equation 6:

$$\Delta G^* = -RT \times Ln (55.5 \times K) \qquad (6)$$

Where K is the adsorption equilibrium constant and 55.5 is the water concentration in mol/l.
ΔG^* = -25.86KJ/mol at 25°C this indicates the physisorption of the inhibitor on the metal surface and the negative sign indicates the spontaneity of the adsorption process.

Adsorption isotherm:

The laws of adsorbed amount variation are based on the concentration of the inhibitor in the solution at a specific temperature, and it can be described by adsorption isotherms. In the latter, the adsorbed amount of an inhibitor is often expressed by the recovery rate of the metal surface (θ), which represents the number of surface adsorption sites effectively occupied (N) based on the total number of sites (N ') per unit area [28].

The adsorption behavior provides information on the interaction between the adsorbed molecules and their interactions with the electrode surface [29].

It has been reported that the adsorption depends on adsorbent interactions / and in particular the nature of the adsorbed species and the nature of the solid surface [30]. The adsorption Temkin, Frumkin, and Langmuir isotherms were used to represent the green mint oil adsorption on the lead surface. The correlation coefficient, R^2, was used to choose the isotherm that best matches the experimental data. The recovery rate (θ) at different concentrations for the inhibitor tested in 0.1M $Na_2CO_3$was assessed from measurements of polarization.
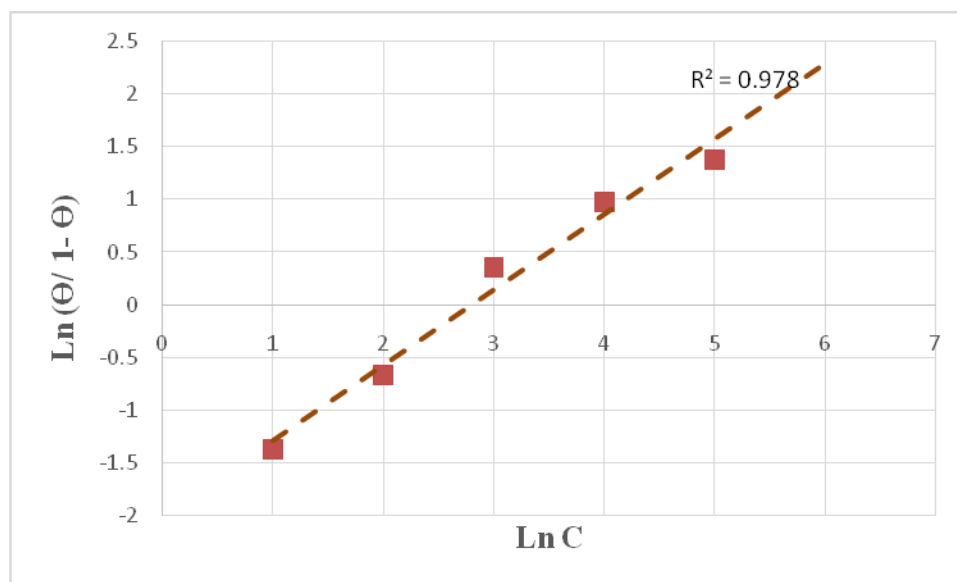
Figure 12 Model Langmuir isotherm for adsorption of green mint essential oil on the surface of the lead in 0.1 M Na_2CO_3 at 25 ° C

The curve representing Ln ($\theta/\theta-1$) as a function of Ln[C], where C is the concentration of inhibitor, is a straight line (Fig. 12) indicating that head sorption of the inhibitor on the surface of the lead plate is according to the Langmuir model (Equation 7)

$$Ln (\theta/1-\theta) = K Ln [C] \quad (7)$$

The strong correlation ($R^2=0.9783$) for the plot of the adsorption isotherm according to Langmuir confirms the validity of this approach.

Conclusion

The results of this study can be concluded as follows:

- The mint essential oil is an effective inhibitor of the corrosion of lead in 0.1 M Na_2CO_3 solution. The efficiency of the mint essential oil increases with the concentration, and can reach 80% at 2000 ppm.
- The results of polarization studies indicate that mint essential oil acts as mixed inhibitor with cathodic predominance.
- The electrochemical impedance spectroscopy technique shows that the adsorption of green mint essential oil on lead surface increases the transfer resistance to 1254.1 KΩ. Cm^2 and reduces the ability of the double layer.
- The adsorption of green mint essential oil on lead in 0.1M Na_2CO_3 solution is of a physical type, it is according to the Langmuir adsorption isotherm, with a high correlation coefficient.

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