

## Use of *Salvia Officinalis* as Green Corrosion Inhibitor for Carbon Steel in Acidic Media

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A study of *Salvia officinalis* as corrosion inhibitor of 1018 carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> has been carried out by using gravimetric and electrochemical tests. Electrochemical techniques included potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements (EIS). Testing temperatures included 25, 40 and 60°C. It was found that *Salvia officinalis* acts as a good corrosion inhibitor for carbon steel with its efficiency increasing with the concentration and decreasing with the testing temperature. Polarization curves showed that both corrosion and passivation current density values were lowered by almost one order of magnitude and therefore that *Salvia officinalis* acts as an anodic type of inhibitor physically absorbed on the steel surface by following a Langmuir type of adsorption isotherm. Long term tests indicated that the inhibitor efficiency increase with time up to 12 hours, and after this time the inhibitor starts to be desorbed from the metal, decreasing its efficiency. The inhibitory properties were due to the presence of compounds such as carboxylic acid and hydroxyl group in the inhibitor structure.

**Keywords:** corrosion, carbon steel, green inhibitor

### 1. INTRODUCTION

The combat against corrosion is a task that for a long time has been undertaken by many scientists and engineers. One of the most widely used practices for this is the use of corrosion inhibitors, both organic and inorganic. Use of many inorganic inhibitors, particularly those containing phosphate, chromate and other heavy metals are now being gradually restricted by various environmental regulations. Many organic inhibitors are also been reported as toxic and environmentally harmful. As a result, researchers are now examining other possible ways, and

designing of environmental friendly bio-compatible green corrosion inhibitors. This has motivated many researchers to focus on the need to develop cheap, non-toxic and environmentally benign natural products such as leaves, fruits or seeds extracts, which can be used as corrosion inhibitors. It can be found in the literature a big amount of research works related with the use of natural products extracts to be used as “green” corrosion inhibitors due to the presence of complex organic species such as tannins, alkaloids, carbohydrates and proteins as well as their acid hydrolysis products [3-20]. The use of these natural products is more effective and highly environmentally benign compared to organic and inorganic inhibitors used in chemical or any industrial applications.

*Salvia officinalis* (*Salvia* spp.), a popular herb in the mint family (Labiatae), has been a subject of intensive study in the past decades for its antioxidative components. *Salvia officinalis* has been long used in folk medicines for the treatment of all kinds of ailments, but to most people it is better known as an additive used in the preparation of different types of foods. Several studies have shown sage to be one of the sources of some potent antioxidant. The antioxidant properties were found to be related to the presence of rosmarinic and carnosic acids [21]. Different studies on *Salvia officinalis* [22, 25] have revealed the presence of a large number of diterpenoids and phenolic acids including a number of novel cafeic acid, metabolites such as sagerinic acid and sagecoumarin, but comparably few flavonoids and phenolic glycosides. The essential oil and flavourants of *Salvia officinalis* are used as basic material for various food, cosmetic and pharmaceutical preparations. *Salvia officinalis* antioxidants can be used as an alternative to the well-known rosemary antioxidants for the protection and preservation of certain food and nutraceutical products. Thus, the goal of this work is to study the use of *Salvia officinalis* as green inhibitor for the corrosion of carbon steel in acid environment.

## 2. EXPERIMENTAL PROCEDURE.

Dried *Salvia officinalis* leaves were soaked in methanol during 24 h and used as a stock solution and used then for preparation of the desired concentrations by dilution. The resulting extract was used as a stock solution and characterized by FTIR and UV-VIS techniques. Weight loss experiments were carried out with carbon steel rods 2.5 cm length and 0.6 cm diameter abraded with fine emery paper until 1200 grade, rinsed with acetone, and exposed to the aggressive solution during 72 h. After a total time of exposition of 72 hours, specimens were taken out, washed with distilled water, degreased with acetone, dried and weighed accurately. Aggressive solution, 0.5 M H<sub>2</sub>SO<sub>4</sub> was prepared by dilution of analytical grade H<sub>2</sub>SO<sub>4</sub> with double distilled water. Tests were performed by triplicate at room temperature (25 °C), 40 and 60 °C by using a hot plate. Corrosion rates, in terms of weight loss measurements, ΔW, were calculated as follows:

$$\Delta W = (m_1 - m_2) / A \quad [1]$$

were  $m_1$  is the mass of the specimen before corrosion,  $m_2$  the mass of the specimen after corrosion, and  $A$  the exposed area of the specimen. For the weight loss tests, inhibitor efficiency, IE, was calculated as follows:

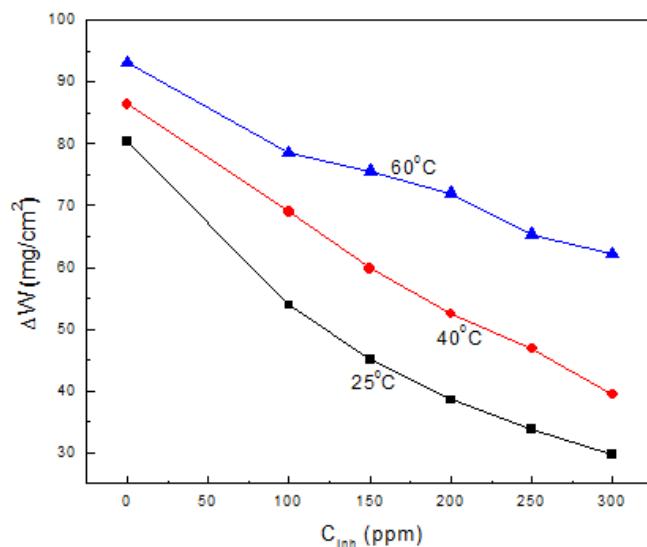
$$IE (\%) = 100 (\Delta W_1 - \Delta W_2) / \Delta W_1 \quad [2]$$

were  $\Delta W_1$  is the weight loss without inhibitor, and  $\Delta W_2$  the weight loss with inhibitor. Specimens were removed, rinsed in water and in acetone, dried in warm air and stored in a dessicator. Specimens were weighed in an analytical balance with a precision of 0.1 mg. Electrochemical techniques employed included potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements, EIS. In all experiments, the carbon steel electrode was allowed to reach a stable open circuit potential value,  $E_{corr}$ . Polarization curves were recorded at a constant sweep rate of 1 mV/s at the interval from -1000 to +1500 mV respect to the  $E_{corr}$  value. Measurements were obtained by using a conventional three electrodes glass cell with two graphite electrodes symmetrically distributed and a saturated calomel electrode (SCE) as reference with a Luggin capillary bridge. Corrosion current density values,  $I_{corr}$ , were obtained by using Tafel extrapolation. Inhibitor efficiency were calculated by using following equation:

$$IE (\%) = 100 (I_{corr1} - I_{corr2}) / I_{corr1} \quad [3]$$

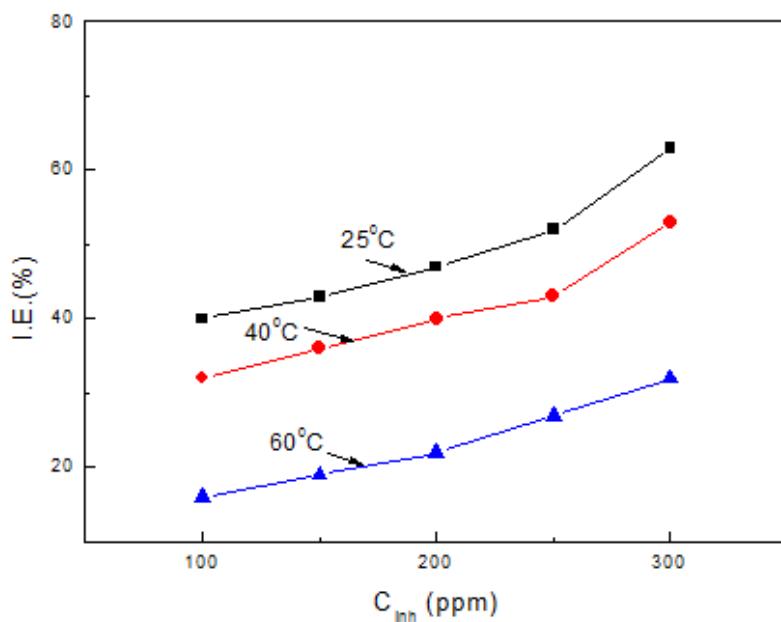
were  $I_{corr1}$  and are  $I_{corr2}$  the corrosion current density without and with inhibitor, respectively. Electrochemical impedance spectroscopy (EIS) tests were carried out at  $E_{corr}$  by using a signal with amplitude of 10 mV in a frequency interval of 50 mHz-100 KHz. An ACM potentiostat controlled by a desk top computer was used for the polarization curves, whereas for the EIS measurements, a model PC4 300 Gamry potentiostat was used.

### 3. RESULTS AND DISCUSSION

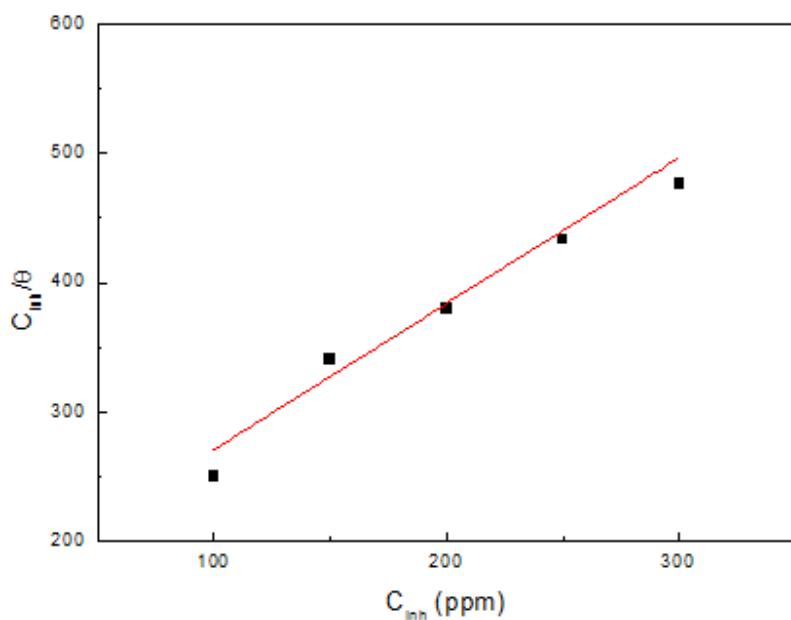


**Figure 1.** Effect of *Salvia officinalis* concentration in the weight loss results for 1018 carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25, 40 and 60°C.

The effect of *Salvia officinalis* concentration on the weight loss for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at the three different testing temperatures is shown in Fig.1, where it can be seen the effect of the inhibitor, since , at a constant temperature, the weight loss decreases with increasing the inhibitor concentration, reaching the lowest weight loss with the addition of 300 ppm of inhibitor. As the temperatures increases, the weight loss increases, indicating a degradation of the inhibitor with the temperature.



**Figure 2.** Effect of *Salvia officinalis* concentration in the inhibitor efficiency values for 1018 carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different temperatures.



**Figure 3.** Langmuir adsorption plots for 1018 carbon steel in absence and presence of different concentrations of *Salvia officinalis* extract in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Inhibitor efficiency increases with the inhibitor concentration, reaching its highest value, 63%, with inhibitor doses of 300 ppm, Fig. 2, but it decreases with increasing the temperature, which indicates that the decrease in the corrosion rate is due to the inhibitor adsorption on the steel surface. In order to evaluate the form that the inhibitor molecules are absorbed onto the metal surface, different absorption isotherms, including Tempkin, Langmuir, Frumkin and Flory-Huggins were used, but, as it can be seen in Fig. 3, the Langmuir type of adsorption isotherm had the best data fitting, with an  $R^2 = 0.94$ , which indicates that *Salvia officinalis* are adsorbed on to the metal surface following this type of adsorption isotherm. Correlation between surface coverage ( $\theta$ ) defined by IE/100 and the inhibitor concentration ( $C_{inh}$ ) can be represented by the Langmuir adsorption isotherm, the isotherm is given by [26]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + \frac{C_{inh}}{K_{ads}} \quad [4]$$

where  $K_{ads}$  is the equilibrium constant for the adsorption-desorption process constant,  $C_{inh}$  is the concentration of the inhibitor and ( $\theta$ ) the surface coverage values obtained from the weight loss measurements for various inhibitor concentrations. Langmuir adsorption isotherm assumes that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species [27].

**Table 1.** Electrochemical parameters obtained from the polarization curves.

$C_{inh}$ (ppm)	$E_{corr}$ (mV)	$I_{corr}$ (mA/cm <sup>2</sup> )	$I_{pas}$ (mA/cm <sup>2</sup> )	$\beta_a$ (mV dec)	$\beta_c$ (mV/dec)	IE (%)
0	-536	0.33	0.16	40	192	--
100	-441	0.16	0.13	28	200	51
150	-450	0.11	0.12	32	185	66
200	-453	0.08	0.12	36	161	76
250	-415	0.04	0.05	38	140	85
300	-390	0.01	0.03	42	117	96

The Gibbs standard free energy of adsorption for the inhibitor was estimated by using the equation [28-29]:

$$\Delta G_{ads}^\circ = -RT \ln K_{ads} \quad [5]$$

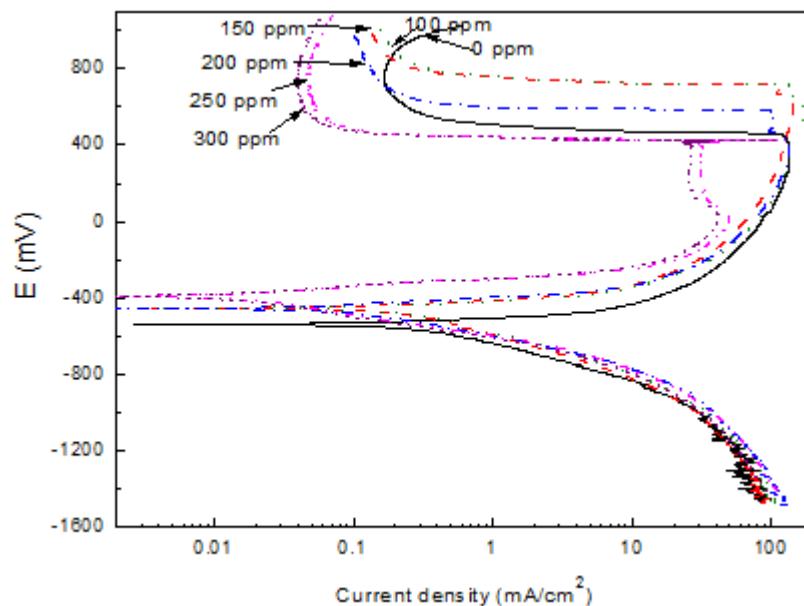
and a value for  $K_{ads}$  of 6.70 was obtained, whereas for  $\Delta G_{ads}^\circ$  the calculated value was -19.52 KJ·mol<sup>-1</sup>, therefore the  $\Delta G_{ads}^\circ$  value is lower than -20 KJ·mol<sup>-1</sup>. Accordingly, if  $\Delta G_{ads}^\circ < -20 \text{ KJ} \cdot \text{mol}^{-1}$  the undergoing process is physisorption and that those above such relative limit of -40 KJ·mol<sup>-1</sup> means that a chemisorption process is under control. For the case considered in

this work, it is possible to state that an electrostatic interaction takes place between the inhibitor molecules and the metallic surface through a physisorption process.

**Table 2.** Effect of *Salvia officinalis* concentration on the electrochemical parameters obtained from the EIS measurements.

$C_{inh}$ (ppm)	$R_s$ (Ohm cm $^2$ )	$R_{ct}$ (Ohm cm $^2$ )	$C_{dl}$ (F/cm $^2$ )	IE (%)
0	4	73	5.5E-05	--
100	19	178	4.2E-5	58
150	20	226	2.8E-05	67
200	21	230	2.6E-05	69
250	21	325	2.4E-05	77
300	22	360	2.2E-05	80

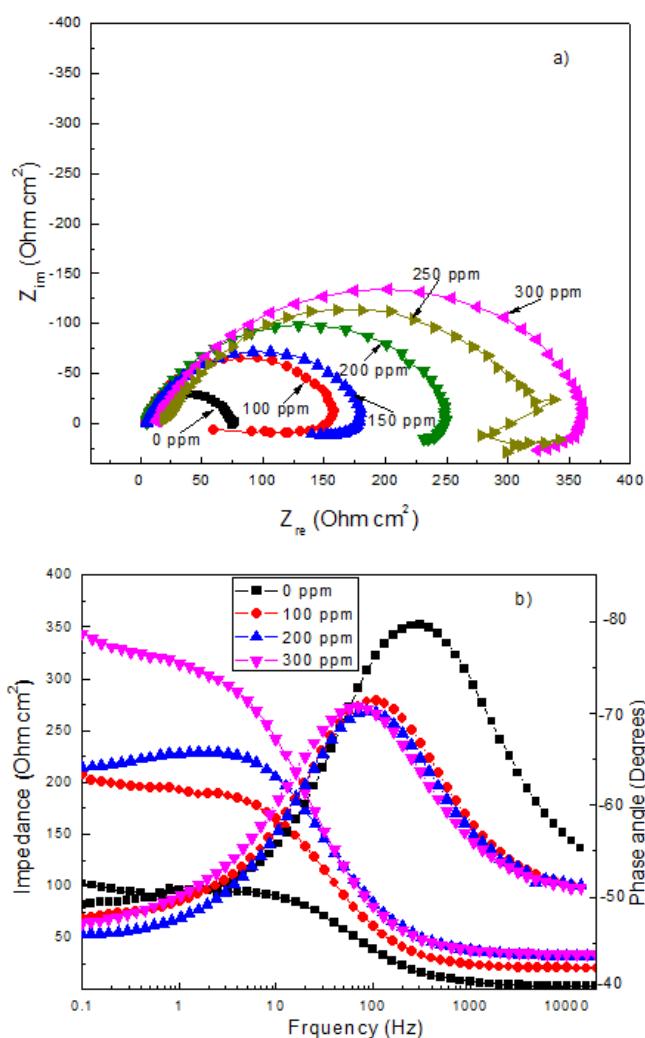
Polarization curves for carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentration of *Salvia officinalis* at 25°C are shown in Fig. 4.



**Figure 4.** Effect of *Salvia officinalis* concentration on the polarization curves for 1018 carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25°C.

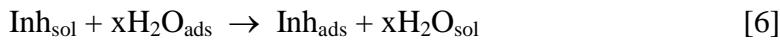
This figure shows that in all cases, regardless of the presence of inhibitor, steel shows an active passive behavior with a passive current density value,  $I_{pas}$ , similar to the corrosion current density for each case. For the blank, uninhibited solution, the anodic current density increases as the applied potential is made more anodic, until a passive region is reached at a passivation potential,  $E_{pas}$ , close

to 640 mV. At this potential, the passive current density remains more or less constant with a further increase in the anodic potential until 900 mV where this passive film is broken and the anodic current density starts to increase. As the inhibitor is added, the  $E_{corr}$  value is shifted towards nobler values and the  $I_{corr}$  value is decreased, reaching its lowest value when 300 ppm of *Salvia officinalis* is added. The passive current density is decreased with the addition of the inhibitor also, reaching a lowest value with 300 ppm of *Salvia officinalis*, but there was not a clear effect on the passivation potential. The cathodic current density practically remained unaffected with the addition of the inhibitor, but the anodic current density was decreased when the inhibitor was added. Electrochemical parameters obtained from the polarization curves are summarized in table 2, where it can be seen that the inhibitor efficiency increased with increasing the inhibitor concentration, reaching its highest value, 96 %, with addition of 300 ppm of inhibitor. Cathodic Tafel slopes remained virtually the same with the addition of *Salvia officinalis*, but the anodic slope was decreased, indicating that *Salvia officinalis* acts as an anodic type of inhibitor.

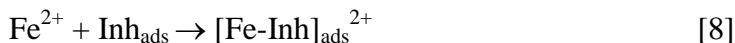
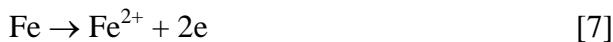


**Figure 5.** Effect of *Salvia officinalis* concentration on the a) Nyquist and b) Bode plots for 1018 carbon steel in 0.5 M  $\text{H}_2\text{SO}_4$  at 25°C.

Anodic type of inhibitors react with the environment to form an insoluble, external, protective, passive film, which protects the metal from further corrosion. It is generally accepted that the first step during the adsorption of an organic inhibitor on a metal surface usually involves replacement of water molecules absorbed on the metal surface.

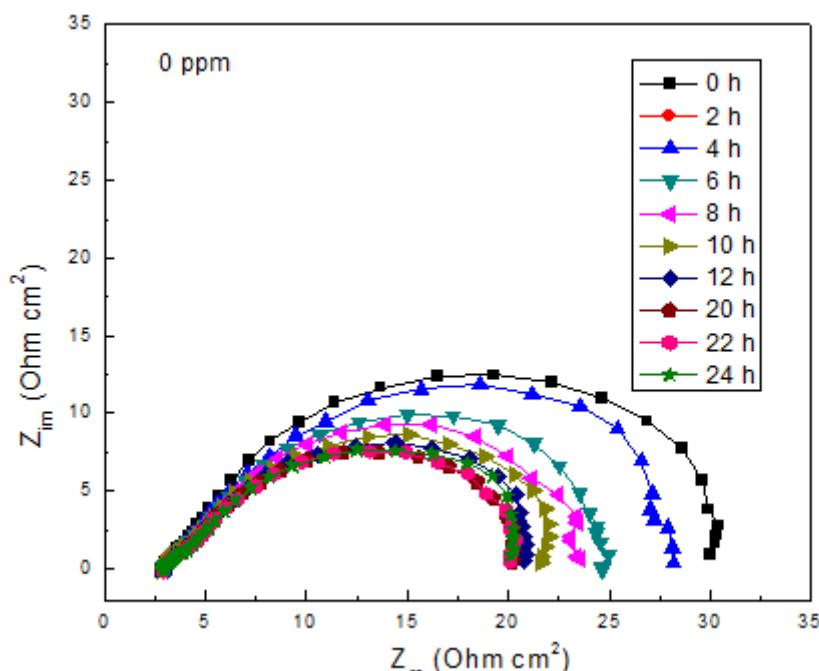


The inhibitor may then combine with freshly generated  $\text{Fe}^{2+}$  ions on steel surface, forming metal-inhibitor complexes [28, 29]:



The resulting complex, depending on its relative solubility, can either inhibit or catalyze further metal dissolution or increase its corrosion rate. At low concentrations the amount of *Salvia officinallis* is insufficient to form a compact complex with the metal ions, so that the resulting adsorbed intermediate will be readily soluble in the acidic environment. But at relatively higher concentrations more *Salvia officinallis* molecules become available for complex formation, which subsequently diminishes the solubility of the surface layer, leading to improve the inhibition of metal corrosion.

Nyquist and Bode plots for carbon steel in 0.5 M  $\text{H}_2\text{SO}_4$  at different inhibitor concentrations at  $25^{\circ}\text{C}$  are shown in Fig. 5. For the blank, uninhibited solution, Nyquist plot describe a single, depressed capacitive-like semicircle at all frequency values, with its center in the real axis, indicating that the corrosion process is under charge transfer control from the metal to the electrolyte through the double electrochemical layer.



**Figure 6.** Change of the Nyquist diagram with time for 1018 carbon steel in uninhibited 0.5 M  $\text{H}_2\text{SO}_4$  solution at  $25^{\circ}\text{C}$ .

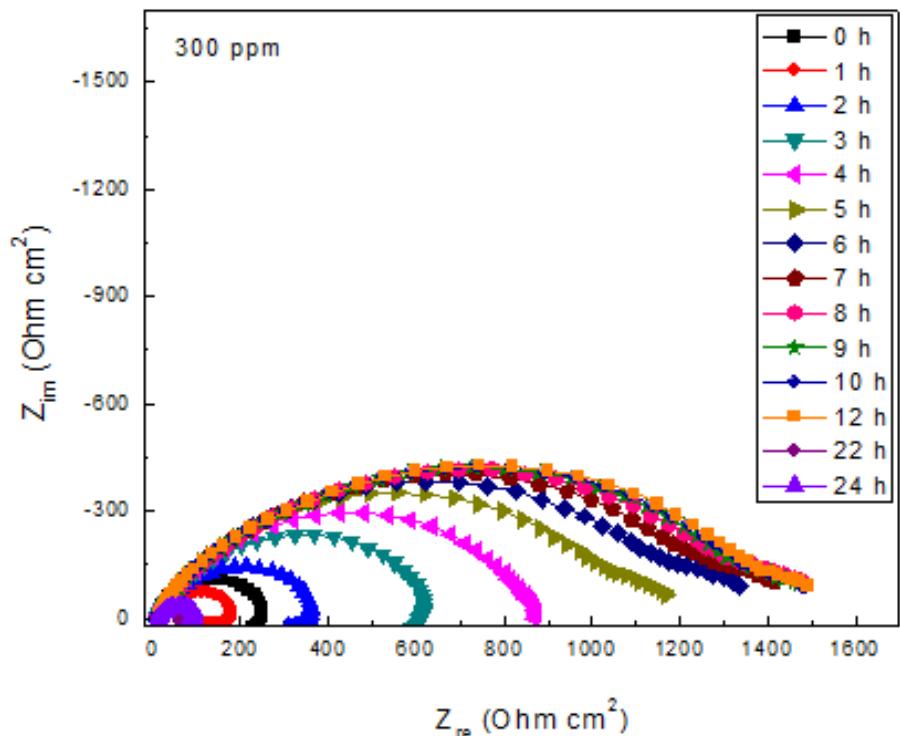
When the *Salvia officinallis* is added to the electrolyte, Nyquist data describe a capacitive loop at high and intermediate frequencies and a second, inductive loop at lower frequencies. The first loop is related to the charge transfer, and the second inductive loop indicates that now the corrosion process is now under the control of the adsorption-desorption of an intermediate species [30]. As *Salvia officinallis* concentration increases, the capacitive semicircle diameter increased, reaching its highest value with the addition of 300 ppm of inhibitor. Bode plot, on the other hand, Fig. 5 b, shows that the addition of *Salvia officinallis* led to an increase in the electrode impedance, and thus, a decrease in the corrosion rate. However, the absence of linear log Z relations with a slope of -1 (especially in the case of an uninhibited system) and the departure of phase angle at intermediate frequencies from 90<sup>0</sup> shows that the circuit tends to the resistive behavior [31]. Bode plot in the frequency-phase angle format shows a peak only which shifts towards lower frequency values as the inhibitor concentration increases, indicating that in presence of *Salvia officinallis* the presence of a more protective passive formed film by the inhibitor.

Since the semicircle diameter from the Nyquist plots corresponds to the charge transfer resistance,  $R_{ct}$ , which is inversely proportional to the corrosion rate, values for  $R_{ct}$  and  $C_{dl}$ , the capacitance of the double electrochemical layer, were calculated, and the results are given in table 2, together with the inhibitor efficiency values obtained according to:

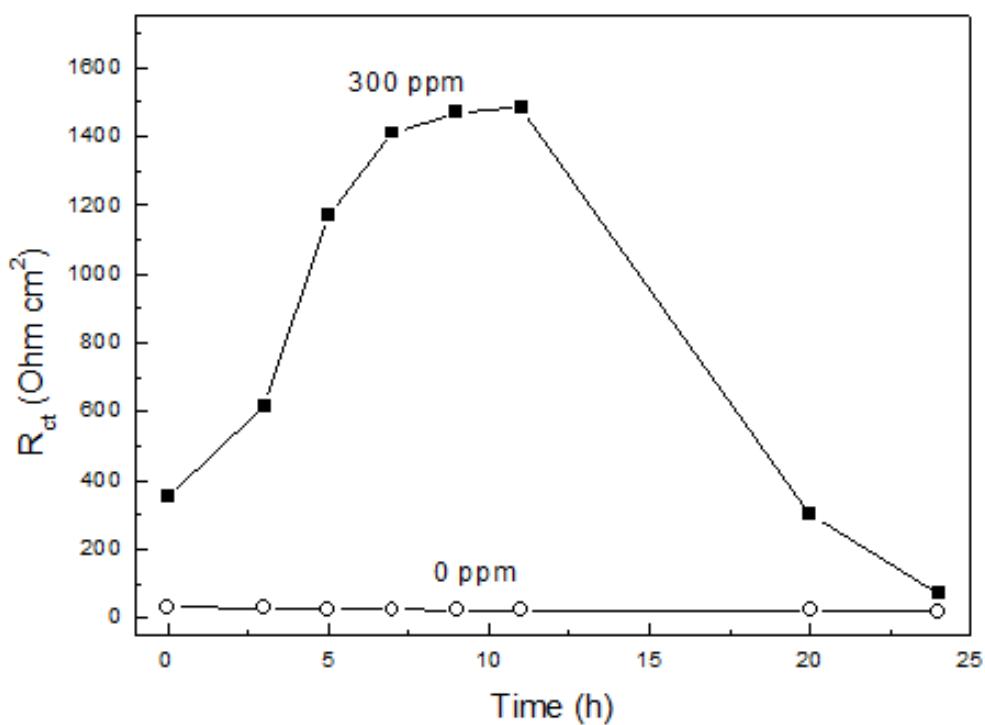
$$IE (\%) = 100 (R_{ct,i} - R_{ct,b}) / R_{ct,i} \quad [9]$$

where  $R_{ct,b}$  is the charge transfer resistance without inhibitor and  $R_{ct,i}$  is the charge transfer resistance with inhibitor. As shown in table 2, reveals that  $R_{ct}$  values increased with increasing inhibitor concentration, bringing, thus, a reduction in the corrosion rate. On the other hand, the values of  $C_{dl}$  decreased with an increase in *Salvia officinallis* concentration. This was a result of an increase in the surface coverage by the inhibitor, which led to an increase in IE%, which suggests that the inhibitor species perform by adsorption at the metal/solution interface [32,33].

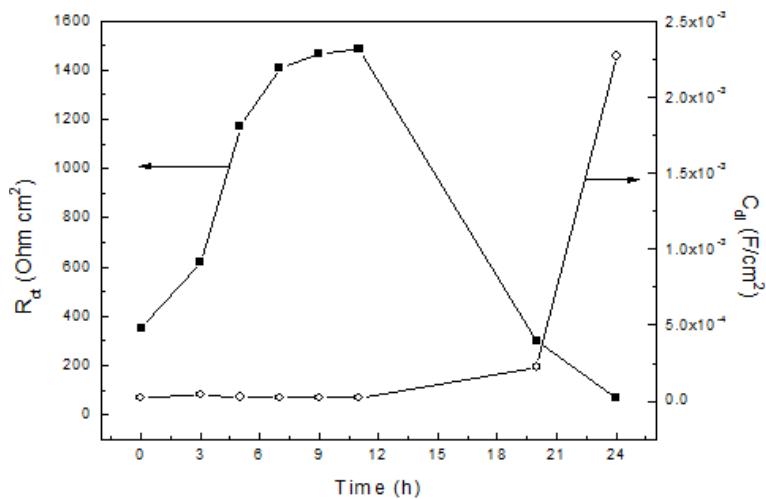
Since it is very important to know for how long time the inhibitor remains on the surface of the metal surface, some long-term EIS tests were performed in both uninhibited and inhibited solution containing 300 ppm of *Salvia officinallis* and the results are shown in Figs. 6 -7 respectively. For the blank, uninhibited solution, Fig. 6 shows that the semicircle diameter decreased continuously as time elapsed, and thus, an increase in the corrosion rate, indicating the non-protective nature of the formed corrosion products. On the other hand, for the solution containing 300 ppm of *Salvia officinallis*, Fig. 7, shows that the semicircle diameter increases with time up to 12 hours of exposition to the aggressive solution, with a decrease in the corrosion rate. After 12 hours of exposure to the solution, the semicircle diameter starts to decrease, which indicates a desorption of the corrosion products complex formed on the metal surface, with an increase in the corrosion rate. Whereas the  $R_{ct}$  value for the uninhibited solution decreased from 30 to 20 ohm cm<sup>2</sup> after 24 hours of exposition, that for the solution containing 300 ppm of inhibitor increased from 360 to 1500 ohm cm<sup>2</sup> after 12 hours, Fig. 8, indicating the protective nature of *Salvia officinallis*.



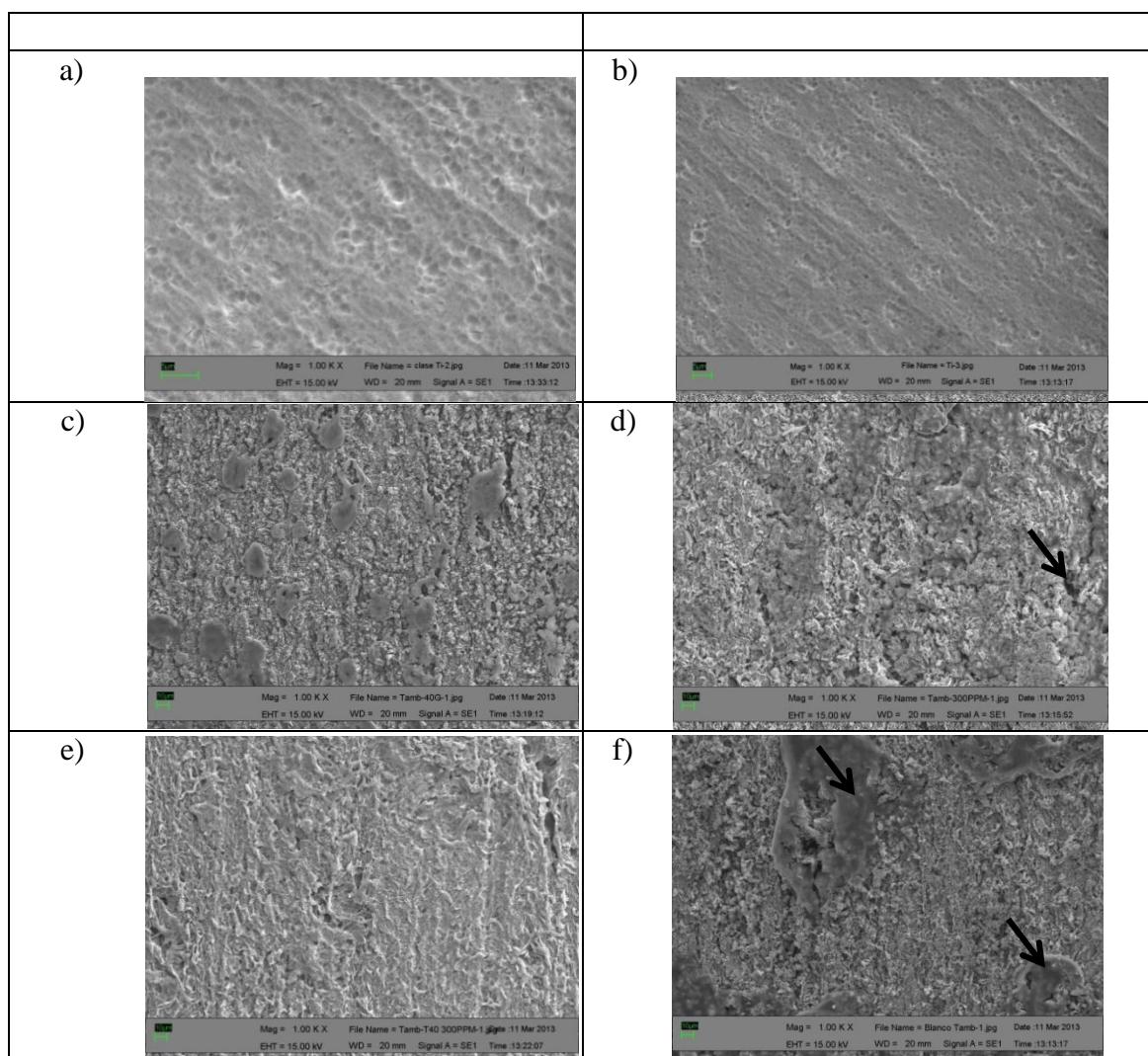
**Figure 7.** Change of the Nyquist diagram with time for 1018 carbon steel in 0.5 M  $\text{H}_2\text{SO}_4$  solution at  $25^\circ\text{C}$  containing 300 ppm of *Salvia officinalis*.



**Figure 8.** Change of the  $R_{\text{ct}}$  value with time for 1018 carbon steel in 0.5 M  $\text{H}_2\text{SO}_4$  solution at  $25^\circ\text{C}$  containing 0 and 300 ppm of *Salvia officinalis*.



**Figure 9.** Change of the  $R_{ct}$  and  $C_{dl}$  values with time for 1018 carbon steel in  $\text{H}_2\text{SO}_4$  solution at  $25^\circ\text{C}$  containing 300 ppm of *Salvia officinalis*.

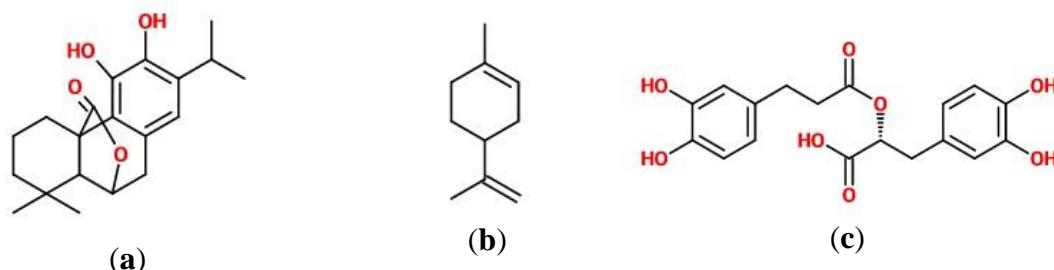


**Figure 10.** Micrographs of carbon steel corroded in 0.5M  $\text{H}_2\text{SO}_4$  at  $25^\circ\text{C}$  (a and b),  $40^\circ\text{C}$  (c and d) and  $60^\circ\text{C}$  (e and f) containing 0 ppm (a, c and e) and 300 ppm (b, d and f) of *Salvia officinalis*.

On the other hand, Fig. 9 shows the evolution of  $R_{ct}$  and  $C_{dl}$  values as time elapses for carbon steel immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 300 ppm of *Salvia officinalis*. The double-layer capacitance was calculated from the equation below:

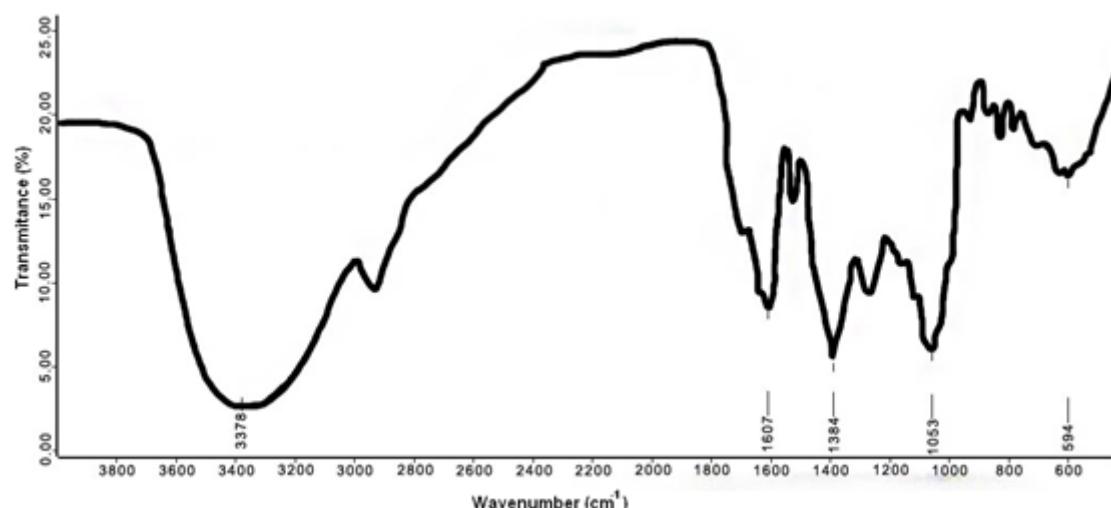
$$C_{dl} = (2\pi f_{max} R_{ct})^{-1} \quad [10]$$

where  $f_{max}$  is the frequency value at which the imaginary component of the impedance is maximal. It is clear the increase in the  $R_{ct}$  value up to 12 hours of exposure to the aggressive solution, and a decrease in the capacitance value. This is due to the adsorption of the inhibitor molecules on the steel surface displacing the aggressive molecules and forming a film which protects the metal from further corrosion. However, after some time, inhibitor molecules starts to be desorbed from the metal, with an increase in the corrosion rate.



**Figure 11.** Chemical structure of some compounds found in *Salvia officinalis* showing a) Carnosol, b) Limonene and c) Rosmarinic acid.

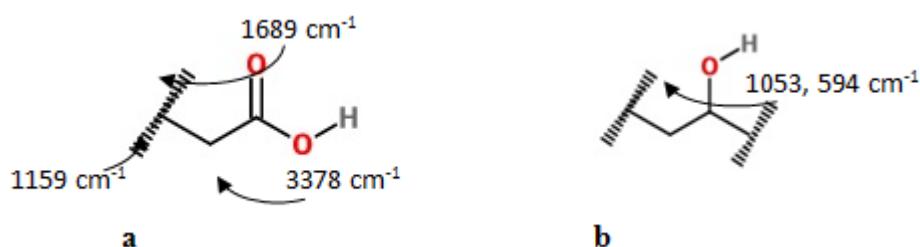
To establish whether inhibition is due to the formation of an organic film on the metal surface, scanning electron micrographs were taken.



**Figure 12.** Infrared spectrum of pure *Salvia officinalis* extract.

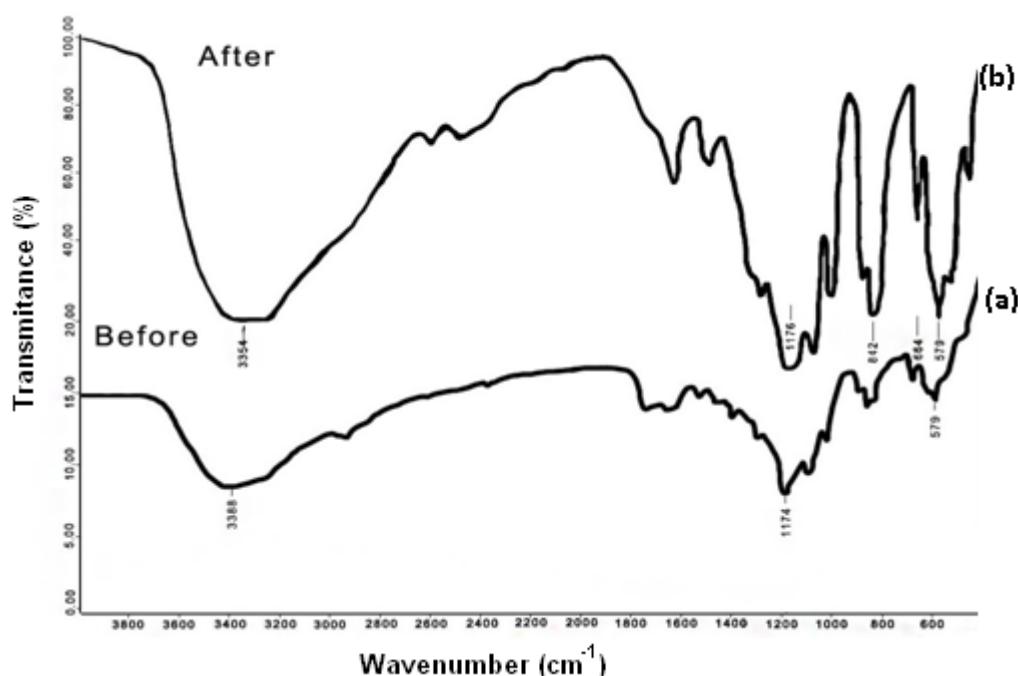
Fig. 10 shows the SEM micrograph of carbon steel surface before and after of the immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C with and without corrosion inhibitor. It is clear that the steel immersed in the uninhibited acidic solution suffered from a more severe damage than that in presence of *Salvia officinalis*. The film formed on the steel in absence of *Salvia officinalis* has more cracks and pits and porous than that formed in presence of the inhibitor, which indicates that the corrosion protection in the inhibited solution is due to the formation of a compact, adherent film formed by the molecules of the inhibitor.

In order to have a better idea of which components of this plant extract are responsible for the decrease in the corrosion rate of carbon steel, an FTIR analysis was performed. *Salvia officinalis* contain mainly terpenes and cinnamic acids as show in Fig. 11.

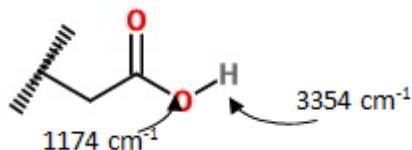


**Figure 13.** Signal assignation for a) carboxylic acid and b)hydroxyl group.

These compounds have in their structures functional groups such as carboxylic acids, secondary and primary alcohols groups, double bonds and aromatics rings. These groups could be found in the infrared spectrum shown in Fig. 12.



**Figure 14.** Infrared spectroscopy of methanol extract from *Salvia officinalis* before and after the corrosion test.



**Figure 15.** Signal assignation for carboxylic acid after the corrosion test.

The signals at 3378, 1689 and 1159  $\text{cm}^{-1}$ , could be assigned to carbonyl acid group (Fig. 13 a). The bending vibration of the hydroxyl group was found in a good agreement with the observed typical spectra ( $3370 \text{ cm}^{-1}$ ) such as intense and wide signal. At 1053 and 594  $\text{cm}^{-1}$  there was evidence of and hydroxyl group from alcohol group (Fig. 13 b). And the last signals could we assigned to double bonds ( $1607 \text{ cm}^{-1}$  to C=C), aromatic ring ( $1521 \text{ cm}^{-1}$  to C=C of aromatic ring and  $926 \text{ cm}^{-1}$  of C-H aromatic ring) and some aromatic rings could be di-substituted ( $860$  to  $779 \text{ cm}^{-1}$ ). The methanolic extract of *Salvia officinalis* before and after the corrosion test is shown in Fig. 14. The spectrum before the corrosion tests show less signals as compared to that for the pure extract (Fig. 12) which could be explained because the extract made probably some interactions with the free protons in the acid media. Additionally, the signals assigned to the carboxylic acid have been shifted now to 3388, 1725 and  $1174 \text{ cm}^{-1}$ , and the signals for hydroxyl group have been shifted to 1016 and  $579 \text{ cm}^{-1}$  also. Even more, a new signal appears at  $1087 \text{ cm}^{-1}$ , which is an evidence of a new interaction between the oxygen through a hydrogen bond. Also, some signals towards the end of the spectrum which correspond to double bonds and aromatic rings were observed.

#### 4. CONCLUSIONS

All the above results indicate that *Salvia officinalis* is a good corrosion inhibitor for 1018 carbon steel in acidic environment. Gravimetric tests showed that inhibitor efficiency increases with the inhibitor concentration but decreases with the testing temperature. *Salvia officinalis* is physically adsorbed on to the metal surface according to a Langmuir type of adsorption isotherm. Both the corrosion and passivation current density values are decreased by almost one order of magnitude when the inhibitor is added, therefore it is an anodic type of inhibitor. As time elapses inhibitor remains on the surface up to certain time, and after that *Salvia officinalis* starts to be desorbed, decreasing its efficiency. The presence of organic compounds such as carboxylic acid and hydroxyl group, which contain heteroatoms, are the responsible for the inhibitory ability of *Salvia officinalis*.

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