Influence of pH on the Use of *Salvia Hispanica* as Green Corrosion Inhibitor for Carbon Steel in Sulfuric Acid

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The use of *Salvia hispanica* as a green corrosion inhibitor for 1018 carbon steel in 0.5 M H_2SO_4 solution at different pH values has been evaluated using weight loss tests, potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements. Solution pH values included 1, 3, 4 and 5. Results have shown that *Salvia hispanica* acts as good, mixed type of inhibitor, with its efficiency increasing with increasing its concentration and with an increase in the solution pH up to a pH value of 4, decreasing when the pH solution is 5. This has been explained in terms of corrosion products film adherence to the metal. Adsorption studies showed that *Salvia hispanica* is chemically adsorbed on to the steel surface following a Langmuir adsorption isotherm.

1. INTRODUCTION

In order to combat corrosion of metals, it is a commonly used practice the use of inhibitors. The following considerations must be taken into account for the choice of an inhibitor: (a) raw materials must be inexpensive, and it should have a convenient synthesis (b) the inhibitor molecule must contain nitrogen, oxygen, sulphur and multiple bonds for its efficiency and (c) a negligible toxicity in the environment [1–4]. It is generally accepted that organic molecules inhibit corrosion via adsorption at the metal-solution interface [5–6]. Regarding organic compounds, it is generally recognized the

existence of two primary mechanisms of adsorption: either by blocking the reaction sites or generating a physical barrier to reduce the diffusion of corrosion species to the metal surface. Different factors such as inhibitor concentration, electrochemical potential at the interface, nature and surface charge of the metal surface, solution chemistry and temperature of the corrosion reaction affect the mode of absorption.

The use of synthetic inhibitors sometimes does not full fill requirements (a) and (c) mentioned above since they are expensive and toxic for both environment and human people. This is the reason why in the last years the use of extracts from seeds, leaves, roots, etc… naturally occurring corrosion inhibitors has been gaining more preference [7-17].*Salvia hispanica* L. (Chia) is a widely used seed in Latin-America, for food, medicine, and oil, especially in Mexico much before the Spanish people came to this country [18, 19]. Chia oil contain several highly unsaturated fatty acids, but the main components are linoleic and α-linolenic acids, two polyunsaturated fatty acids, which cannot be produced in the human body, in addition to myrcetin, quercetin, kaempherol, and caffeic acid which act as potent antioxidants. Hermoso-Diaz et al. [20] evaluated the use of *Salvia hispanica* extract as corrosion inhibitor for 1018 carbon steel in 0.5 M H_2SO_4 and found that *Salvia hispanica* is a good corrosion inhibitor not only for a uniform type of corrosion, but also for localized type of corrosion, and its efficiency increased with increasing its concentration but decreased with increasing the testing temperature. The rate of metal corrosion is greatly affected by temperature and solution pH and their variation is a very useful tool for studying and clarifying the adsorption mechanism of an inhibitor. Thus, the goal of this paper is to evaluate the effect of solution pH on the use of *Salvia hispanica* as corrosion inhibitor for 1018 carbon steel in 0.5 M H_2SO_4.

2. EXPERIMENTAL DETAILS.

2.1 Testing solution

The procedure to obtain methanolic extract of *Salvia hispanica* has been described elsewhere [20]. Aggressive solution consisted of 0.5M of H_2SO_4 and its pH value was adjusted to 1, 3, 4 and 5 by adding drops of o1.0 M NaOH solution. Metal evaluated in this work consisted of 6 mm diameter rods of 1018 carbon steel containing 0.14%C, 0.90% Mn, 0.30%S, 0.030% P and as balance Fe. They were cut in pieces with 15 mm length, encapsulated in commercial epoxy resin. Specimens were ground with 600 grade emery paper, rinsed with water and dried with warm air. For the weight low measurements, they were immersed in solution by triplicate at 0, 100, 200, 400, 600, 800 and 1000 ppm during 72 hours at room temperature. After that period of time, they were taken out, cleaned, washed and weighted to obtain the final weight loss.

2.2 Weigh loss tests

The weight loss was calculated by using the following expression:

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

where m_1 is the initial mass of the specimen, m_2 the final mass of the specimen, and A the exposed area of the specimen. Inhibitor efficiency, IE, was calculated as follows:

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

where ΔW_1 and ΔW_2 are the weight loss without and with inhibitor respectively. After the corrosion tests, specimens were observed in a LEO 1450VP scanning electron microscope (SEM).

2.3 Electrochemical tests

Potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements were used. Encapsulated specimens in commercial polymeric resin were used for these tests. A conventional three electrodes electrochemical cell was used, with a saturated calomel electrode (SCE) as reference whereas as auxiliary electrode a graphite rod was used. Before running the tests, working electrode was allowed to achieve a stable free corrosion potential value (E_{corr}). For polarization tests, specimen was polarized from -800 to + 1500 mV respect the E_{corr} value at a scan rate of 1 mV/s. Corrosion current density values, I_{corr}, were calculated by using Tafel extrapolation method. Electrochemical impedance spectroscopy measurements (EIS) were carried out in a PC4 300 Gamry potentiostat by applying a signal with an amplitude of ±15 mV around the E_{corr} value in an interval frequency 10 KHz-0.5 Hz obtaining 50 points per decade.

3. RESULTS AND DISCUSSION

3.1 Weight loss

Table 1. Weight loss and inhibition efficiency values for 1018 carbon steel corroded in 0.5 M H_2SO_4 solution.

C_{inh} (ppm)		ΔW (mg/cm^2)	I.E. (%)	θ
pH=1	0	0.02597	___	___
	100	0.01453	46.11	0.4611
	200	0.00755	73.23	0.7323
	400	0.0041	84.45	0.8445
	600	0.0033	88.61	0.8861
	800	0.0024	92.33	0.9233
	1000	0.0022	95.57	0.9557
pH=3	0	8.307E-4	___	___
	100	7.69E-4	41.1838	0.4118
	200	7.25E-4	44.4976	0.4449

	400	6.71E-4	48.6428	0.4864
	600	5.29E-4	59.5223	0.5952
	800	5.05E-4	61.3688	0.6136
	1000	4.67E-4	64.2388	0.6423
pH=4	0	6.05E-4	___	___
	100	5.52E-4	13.7479	0.1374
	200	4.89E-4	19.1973	0.1919
	400	5.08E-4	22.0385	0.2203
	600	4.31E-4	26.7069	0.2670
	800	4.41E-4	29.9983	0.2999
	1000	3.44E-4	43.1811	0.4318
pH=5	0	0.00106	_____	____
	100	9.14E-4	8.634	0.086
	200	8.84E-4	13.4039	0.1340
	400	8.46E-4	19.0239	0.1902
	600	8.4E-4	20.615	0.2061
	800	7.41E-4	24.9768	0.2497
	1000	6.56E-4	33.0377	0.3303

The effect of *Salvia hispanica* concentration on the weight loss tests and corrosion inhibition efficiency values for 1018 carbon steel in 0.5 M H_2SO_4 at different pH values is given in table 1, where it can be seen that, at a fixed solution pH, the weight loss decreases with increasing the *Salvia hispanica* concentration. The highest weight losses were obtained at a pH value of 1, and decreased with an increase in the solution pH, obtaining the lowest weight loss at a pH of 4. However, the weight loss increased once again when the solution pH increased up to 5. Inhibitor efficiency values increased with an increase in the *Salvia hispanica* concentration, but it decreased as the solution pH increased, obtaining the lowest value at a pH value of 5. This decrease in the weight loss is due to the absorption of *Salvia hispanica* on the metal surface, and the fact that the inhibitor efficiency increase with increasing its concentration is because the metal surface covered by the metal, θ, increases with its concentration.

To know how the inhibitor is adsorbed on the steel surface, several isotherms (Temkin, Frumkin and Langmuir isotherm) have been tested, but the best fit was obtained for Langmuir isotherm for all the solutions pH values as shown in Fig. 1 [21]. Langmuir isotherm considers uniform activity

over the surface for adsorption to take place and no interaction among adsorbed molecules. The Langmuir isotherm is given by:

$$K_{ads}C_{inh} = \theta/1-\theta \qquad [3]$$

where K_{ads} is the equilibrium constant of adsorption process which is related to the standard free energy of adsorption (ΔG^0_{ads}) by following equation :

$$\Delta G^0_{ads} = RT \ln K_{ads} \qquad [4]$$

where R and T are the universal gas constant and the absolute temperature, respectively. Normally, for ΔG^0_{ads} values less negative than –20 kJ/M are due to attributed to a physical adsorption or to an electrostatic interaction between the charged molecules and the charged metal surface [21].
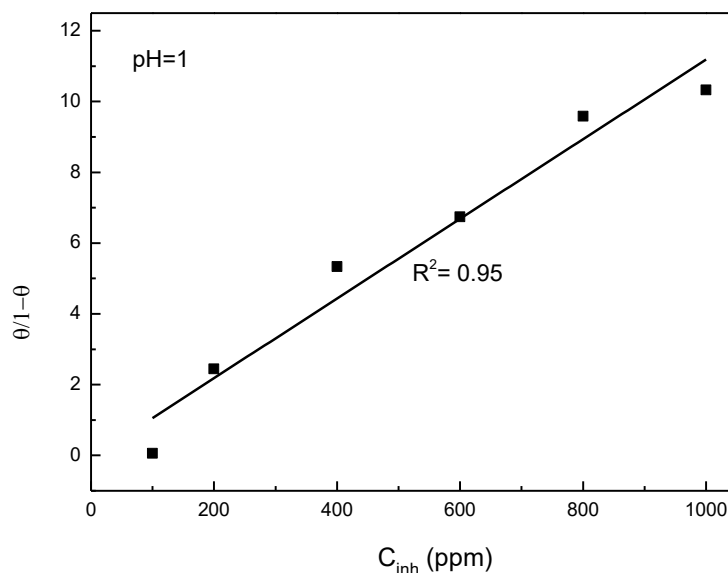
Figure 1. Langmuir type of adsorption isotherm for 1018 carbon steel corroded in 0.5 M H_2SO_4 solution, pH=1, containing *Salvia hispanica*.

On the other side, for ΔG^0_{ads} values more negative than–40 kJ/ M are due to chemical adsorption of the inhibitor, with charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond [22]. Table 2 gives the calculated values of equilibrium constant (K_{ads}) and standard free energy of adsorption of *Salvia hispanica* extract on carbon steel.

Table 2. Values for K_{ads} and ΔG^0_{ad} for obtained from Langmuir type of adsorption isotherm 1018 carbon steel corroded in 0.5 M H2SO4,pH 1, in presence of *Salvia hispanica*.

Solution pH	K_{ads} (L/M)	ΔG^0_{ads} (kJ/ M)
1	987.32	-19.21
3	1200.00	-25.405
4	1404.08	-33.184
5	1030.85	-22.483

It can be seen that the ΔG^o_{ads} values are more negative than -20 kJ/M which means that the adsorption of *Salvia hispanica on carbon steel* is spontaneous and the adsorption type is chemical. The ΔG^o_{ads} becomes less negative whereas the K_{ads} values increase as the pH increase, but it decreases at a ph value of 5, indicating a stronger adsorption of *Salvia hispanica* extract on carbon steel as the solution pH increases, but decreasing at a pH value of 5, affecting its efficiency.

3.2 Polarization curves

As an example of polarization curves, Fig. 2 shows the effect of *Salvia hispanica* concentration on the polarization curves for 1018 carbon steel in 0.5 M H_2SO_4 at a pH values of 3. In this figure it can be seen that for the uninhibited solution and for inhibitor concentrations of 100 and 200 ppm, steel did not show a clear active-passive behavior, but only anodic dissolution and in the cathodic branch a limit current density can be seen, probably due to the oxygen reduction reaction.
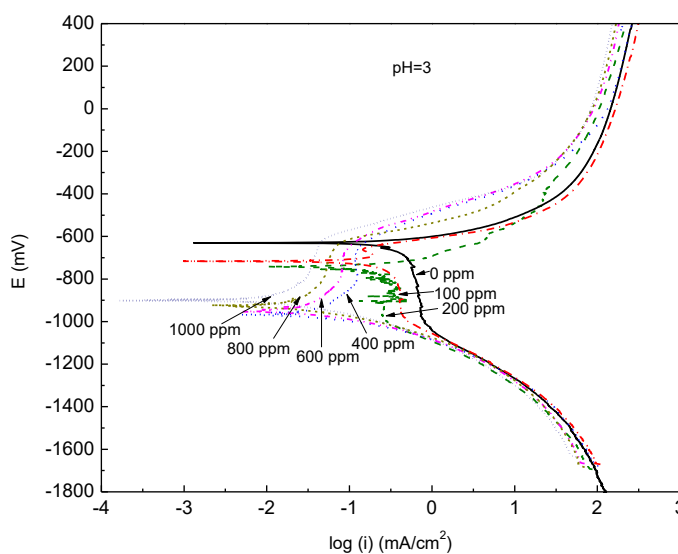

Figure 2. Effect of *Salvia hispanica* concentration in the polarization curves for 1018 carbon steel corroded in 0.5 M H_2SO_4 solution, pH=3.

Table 3. Electrochemical parameters obtained from the polarization curves for 1018 carbon steel corroded in 0.5 M H_2SO_4 solution, pH= 3.

C_{inh} (ppm)	E_{corr} (mv)	I_{corr} (mA/cm^2)	β_c (mV/dec)	β_a (mv/dec)	E.I. (%)	I_{pas} (mA/cm^2)	E_{pit} (mv)
0	-631	0.801	400	135	28	--	--
100	-880	0.575	360	140	38	--	--
200	-741	0.331	223	150	58	--	--
400	-690	0.125	98	235	84	0.312	-640
600	-953	0.038	80	243	88	0.124	-635
800	-927	0.034	84	230	89	0.072	-620
1000	-900	0.016	98	238	95	0.034	-610

Table 4. Electrochemical parameters obtained from the polarization curves for 1018 carbon steel corroded in 0.5 M H$_2$SO$_4$ solution at different pH values, containing 1000 ppm of *Salvia hispanica*.

pH	E$_{corr}$ (mv)	I$_{corr}$ (mA/cm^2)	β$_c$ (mV/dec)	β$_a$ (mv/dec)	I$_{pas}$ (mA/cm^2)	E$_{pit}$ (mv)
1	-950	14	371	387	20	725
3	-900	0.016	98	238	0.034	-610
4	7-957	0.0001	69	188	0.002	-400
5	-990	0.052	59	90.52	0.62	-300
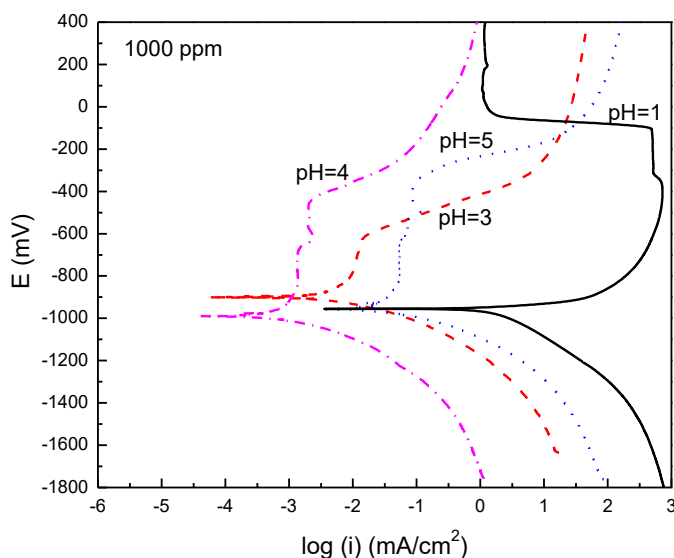
Figure 3. Effect of solution pH in the polarization curves for 1018 carbon steel corroded in 0.5 M H$_2$SO$_4$ containing 1000 ppm of *Salvia hispanica*.

However, for inhibitor concentrations higher than 200 ppm, steel shows a passive zone which starts at the E$_{corr}$ value, the limit cathodic current density disappears and the passive current density value, I$_{pas}$, decreased as the inhibitor concentration increased.

The pitting potential value, E$_{pit}$, remained practically unaffected but the I$_{corr}$ value decreased as the *Salvia hispanica* concentration increased, as can be seen in table 3. On the other side, cathodic Tafel slopes were lowered whereas the anodic ones increased by the addition of *Salvia hispanica*, which indicates that the reduction in the corrosion rate is due to the reduction in the cathodic reactions, such as hydrogen evolution and oxygen reduction. Since the lowest corrosion current density values were obtained with the addition of 1000 ppm of *Salvia hispanica*, the effect of solution pH on the polarization curves for 1018 carbon steel in 0.5 M H$_2$SO$_4$ with the addition of 1000 ppm is shown in Fig. 3. It can be seen that the I$_{corr}$ value, the anodic and cathodic current density values decreased with the increase in the solution pH from 1 up to 4, as shown in table 4, but they increased once again when the pH is further increased to a value of 5. Similar results were obtained with the weight loss tests. For the solution with a pH value of 1, steel displayed a passive region close to 0 mV, almost 1000 mV

more anodic than the E_{corr} value, with a passive zone wider than 400 mV, whereas for the solutions with higher pH values, the passive zone was found a few mV more anodic than the E_{corr} value.

3.3 EIS measurements

The effect of *Salvia hispanica* concentration on the Nyquist and Bode diagrams for 1018 carbon steel in 0.5 M H_2SO_4 solution with pH=3 is given in Fig. 4.
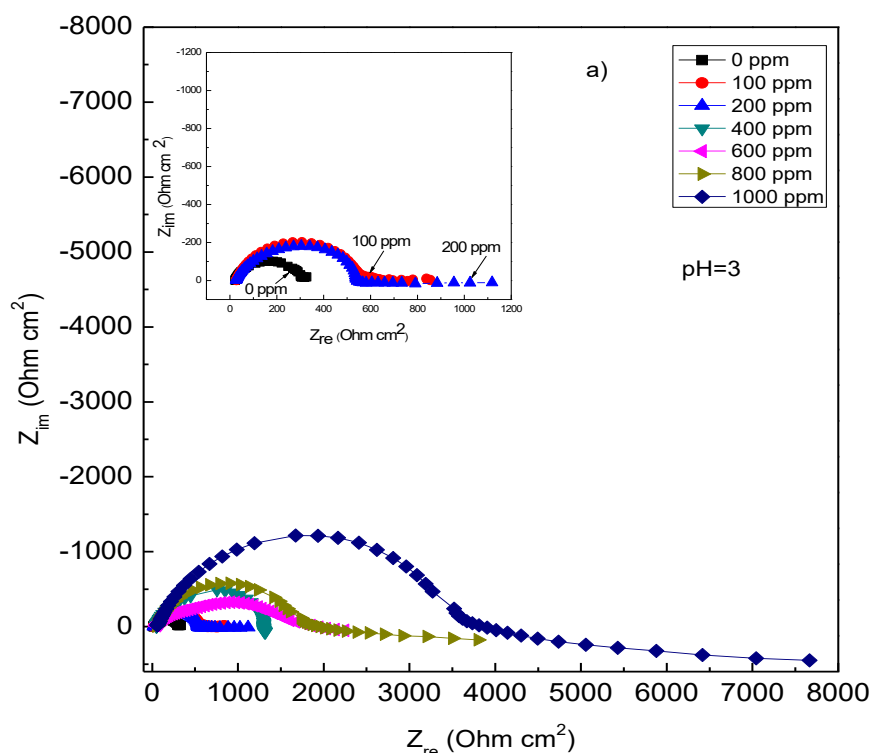

Figure 4. Effect of *Salvia hispanica* concentration in the Nyquist diagrams for 1018 carbon steel corroded in 0.5 M H_2SO_4 solution, pH=3.

It can be seen that Nyquist diagrams, Fig. 4 a, show at all frequency values, a capacitive semicircle, indicating a charge transfer controlled corrosion. The semicircle diameter increases with increasing the *Salvia hispanica* concentration, reaching its highest value with the addition of 1000 ppm. The semicrcle diameter represents the charge transfer resistance, R_{ct}, equivalente to the polarization resistance, R_p, which is inversely proportional to the I_{corr} value. Thus, the highest R_{ct} value obtained with 1000 ppm of *Salvia hispanica* indicates that the I_{corr} value is the lowest at this concentration, corroborating the results obtained with the polarization curves and the weight loss tests. On the other side, Bode diagrams, Fig. 4 b, shows a single peak for all concentrations at phase angle of 60 degrees, and it shifts towards higher frequency values as the inhibitor concentration increases, except at 600 ppm, where two peaks can be observed. The existence of a single peak indicates only

one time constant except at 600 ppm, where the existence of two peaks indicates the existence of two time constants.

Electrochemical parameters such as solution and charge transfer resistance, R_s and R_{ct} respectively, as well as the double layer capacitance and the inhibitor efficiency are given in table 5. It can be seen that the double layer capacitance, C_{dl}, decreases as the inhibitor concentration increases, due to the absorption of the inhibitor on the metal surface and the replacement of the water molecules from the surface, decreasing, thus, the corrosion rate. Inhibition efficiency increases with the inhibitor concentration, as shown by the weight loss tests and polarization curves results also.

Table 5. Electrochemical parameters obtained from Nyquist diagrams for 1018 carbon steel corroded in 0.5 M H_2SO_4 solution, pH= 3.

C_{inh} (ppm)	R_s (ohm cm^2)	R_{ct} (omh cm^2)	Capacitance (F/cm^2)	I.E. (%)
0	4	328	5.3914×10^{-6}	-
100	4	854	1.8636×10^{-6}	61
200	5	1118	1.4235×10^{-6}	70
400	5	1307	1.2425×10^{-6}	74.90
600	5	2244	2.3641×10^{-7}	85.34
800	5	3802	2.0930×10^{-7}	91.37
1000	4	7663	1.8881×10^{-7}	95.71

The effect of solution pH on the Nyquist diagrams for 1018 carbon steel immersed in 0.5 M H_2SO_4 containing 1000 ppm of *Salvia hispanica* is shown in Fig. 5.
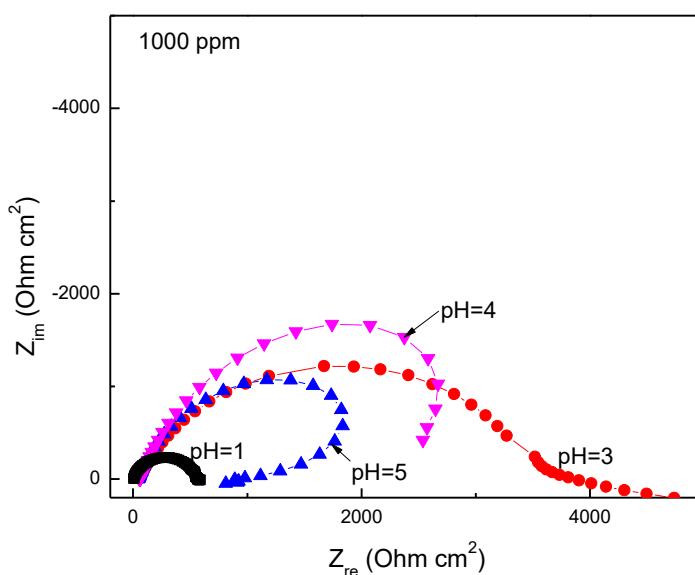

Figure 5. Effect of solution pH in the Nyquist diagrams for 1018 carbon steel corroded in 0.5 M H_2SO_4 containing 1000 ppm of *Salvia hispanica*.

It can be seen that data display a capacitve semicircle at all frequency values, for pH values of 1 and 3, and that the semicircle diameter increases with increasing the solution pH up to 3; at higher solution pH values, the semicircle diameter decreases. For pH values of 4 and 5, data describe a capacitive semicircle at high and intermediate frequency values, whereas at lower frequency values, an inductive loop can be seen, indicating that at these pH values, the corrosion process is under the adsorption/desorption process. Thus, the corrosion process changes with the solution pH. For low pH values such as 1 and 3, the corrosion process is under charge transfer control from the metal surface to the solution through the double electrochemical layer, whereas for pH slightly higher such as 4 and 5, the corrosion process is under the control of the adsorption/desorption of some species at the metal surface. These species could be the ones formed between iron ions, Fe^{2+}, released during the corrosion process, and the inhibitor (Inh) forming a complex such as $[Fe^{2+}\text{-Inh}]_{complex}$ at the metal/solution interface. The adsorption /desorption of these species is the step which controls the corrosion process at pH values of 4 and 5.
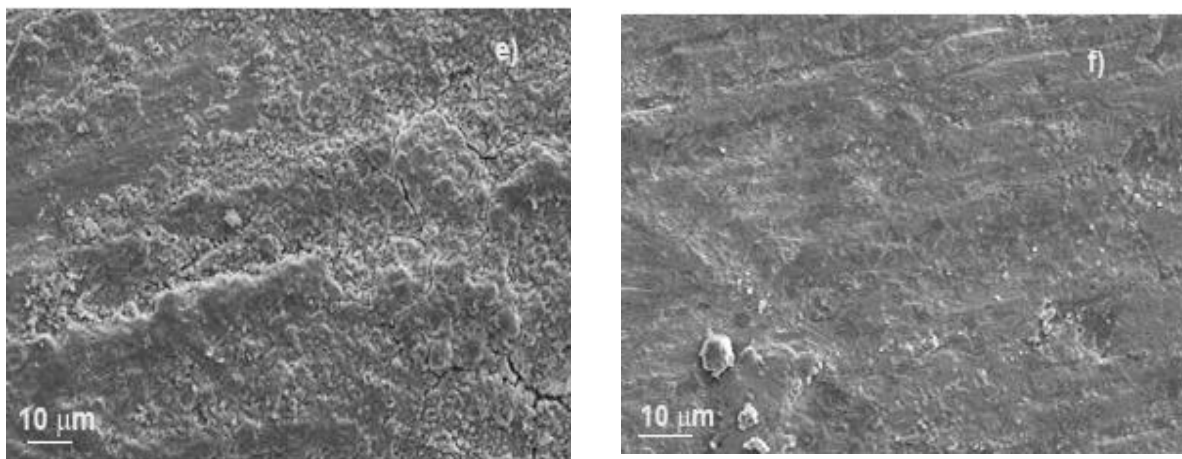
3.4 SEM micrographs
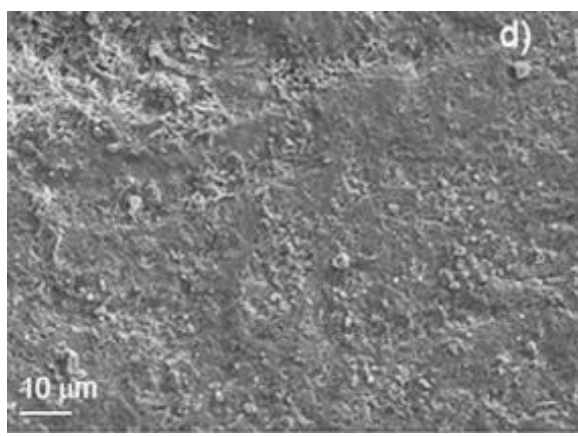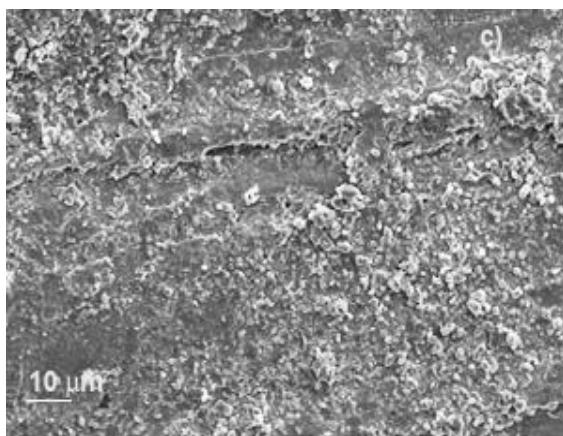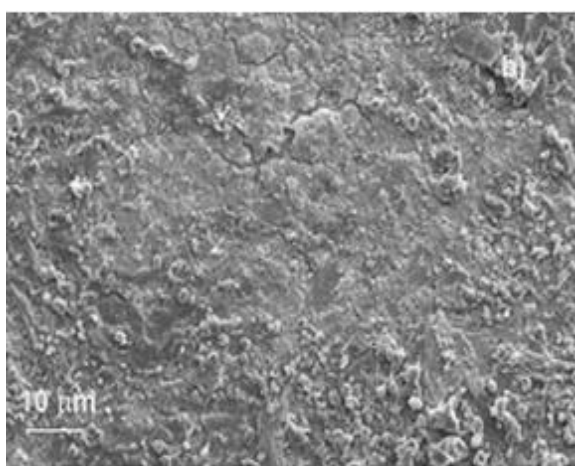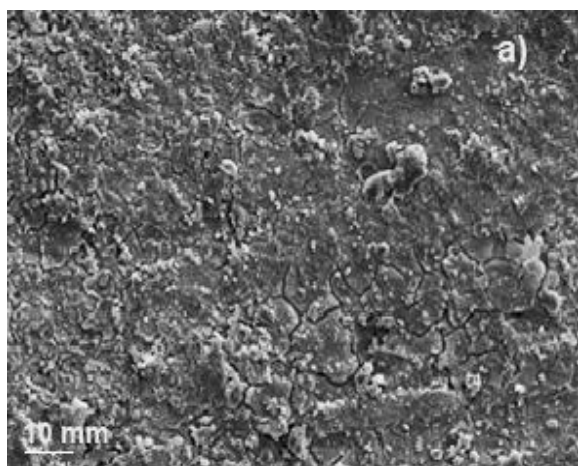
Figure 6. SEM micrographs of corroded specimens in uninhibited 0.5 M H$_2$SO$_4$ solution (a, c, and e) and in 0.5 M H$_2$SO$_4$ solution +1000 ppm of *Salvia hispanica* (b, d and f) at pH=3 (a, b), pH=4 (c, d) and pH=5 (e, f).

SEM micrographs of corroded specimens at the pH values of 3, 4 and 5 with out and with 1000 ppm of *Salvia hispanica* are shown in Fig. 6. It can be seen that, for uninhibited solutions, Fig. 6 a, c and d, corroded specimens show a film with many cracks except at a pH value of 4, but for the inhibited solutions, Fig. 6 b, d and f, the presence of cracks is less evident. It is evident the damaged corrosion products film at pH 3, which indicates the low protectiveness given by this film under these circumstances. The corrosive solution can penetrate to the underlying metal through these cracks, thus, the less protective film is found in a solution with a pH values of 3 and 5, especially for the uninhibited solution. At pH 4 and 5, in the uninhibited solutions, still present defects such as microcracks and porous, but in less amount than at pH 3. The presence of such a defects will affect the adherence of any protective film formed by the inhibitor. Thus, the high corrosion rates found in solutions with pH values of 3 and 5 is due to the formation of a cracked corrosion products film. When inhibitor is added, at pH 3, the formed corrosion products film still have some defects such as micro cracks, Fig. 6 b, and as pH values of 4 and 5, the presence of these defects is much less evident.

It has been reported that the main compounds found in *Salvia hispanica* are linoleic and α-linolenic acids as well as myrcetin, quercetin, kaempherol, and caffeic acid with potent antioxidant activity [23, 24]. These compounds contain heteroatoms in their chemical structure such as C, N and O among others. In addition to this, it has been suggested that many compounds found in natural-occurring inhibitors have a protonated form with a greater tendency of protective barrier formation in the acid environment due to their high tendency to donate electrons which is positively influenced by the acid medium.

These protonated species can be absorbed on to the steel surface to retard the cathodic hydrogen evolution reaction, and thus, decrease the corrosion rate. The adsorption occurs through π-electrons of oxygen atoms present in the caffeic acid decreases the anodic dissolution of 1018 carbon steel [25, 26]. As the constituent molecules contain aromatic rings (π-electrons) and electron releasing groups attached to these aromatic rings, the availability of π−electrons to get linked to the unoccupied

d-orbital of Fe is increased. As the solution pH increases, this tendency to be protonated is lowered and so is the compound ability to donate electrons and, therefore, to form a protective barrier against corrosion [11-15]. This is the reason why at higher pH values such as 5, the inhibition efficiency is greatly decreased.

There are several works in the literature dealing with the effect of pH on the inhibitors performance [27-30]. In all of these works, the inhibitors efficiency increases with an increase in the pH value. As stated in these works, inhibitor performance depends upon the pH solution, among other factors, because it will affect the corrosion mechanism, metal state, inhibitor molecule, i.e. weather it is protonated or deprotonated, and the kind of formed corrosion products. For instance, in a solution with neutral pH, such as 0.5 M NaCl, the corrosion of copper proceeds without the establishment of a protective oxide layer, only with the formation of CuCl, whereas at lower values of pH the formation of CuCl is under a layer of a Cu_2O film. Therefore, if the formed oxide film does not have a good adherence to the metal, the adsorption of the complex formed between inhibitor and metal ions will not be strong enough [31, 32]. Additionally, in low pH solutions, corrosion products normally are thick, porous, and can be dissolved by the environment, making them not protective, whereas in higher pH solutions, the corrosion products are thin, adherent, not soluble, and more protective, where the inhibitor can be adsorbed more easily. Ramde et al. [29] used *Camellia sinensis* extract as corrosion inhibitor for 65 Cu-35 Zn brass in 0.1 M Na_2SO_4 solution at pH values of 4 and 7, finding an increase in the inhibitor protection as the pH value increased. On the other hand, Curkovic et al. [30] use two imidazole-based inhibitors for copper in 0.5 M HCl (pH = 2) and 0.5 M NaCl (pH = 5.6) finding similar results. They explained this improvement in efficiency with an increase in the solution pH to a stronger adherence of the deprotonated inhibitor at high pH values than that for a protonated inhibitor which would exist at acidic solutions. According to data given in table 2, the adsorption constant value increases with an increase in the pH value from 1 to 4, but it decreases when the pH increases up to 5. Micrographs shown in Fig. 6 show that at a pH value of 3 and 5, the film formed on the metal surface present micro cracks, indicating the non-protective nature of these films. Thus, we can say that the increase in the *Salvia hispanica efficiency* from acidic to neutral pH values is related with its adherence to the metal surface.

4. CONCLUSIONS

Salvia hispanica acts as a good corrosion inhibitor for 1018 carbon steel in 0.5 M H_2SO_4 with its efficiency increasing with increasing its concentration, but it decreases with an increase in the solution pH. Electrochemical studies showed that

Salvia hispanica is a mixed type of inhibitor, and that the corrosion process is under charge transfer control for pH values of 1 and 3, whereas at higher solution pH values, the corrosion process is under adsorption/desorption control. Adsorption studies indicated that *Salvia hispanica* is chemically adsorbed on to the steel surface and obey a Langmuir type of adsorption isotherm. The decrease in the corrosion inhibition efficiency with an increase in the solution pH is due to a decrease

in the ability of some of *Salvia hispanica* compounds to be protonated which form corrosion products less adherent than those formed by the deprotonated inhibitor.

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