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Use of EIS and Electrochemical Noise Fractal Analysis to Study *Salvia hispanica* as Green Corrosion Inhibitor for Carbon Steel

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A study on the use of *Salvia hispanica* (Chia) as green corrosion inhibitor for 1018 carbon steel in 0.5 M H_2SO_4 has been carried out by using electrochemical impedance (EIS) and electrochemical noise measurements (EN). Parameters such as polarization and noise resistance were obtained and Hurst exponent and fractal dimension were calculated. Both techniques showed that *Salvia hispanica* acts as good inhibitor since the corrosion rate decreased by more than one order of magnitude with its addition. Hurst exponent and fractal dimension calculations gave very similar results. Inhibitor efficiency was 90% for up to 24 hours of immersion.

Keywords: Acid corrosion, green inhibitor, fractal dimension, Hurst exponent.

1. INTRODUCTION

Carbon steel is widely used in the industry were acids such as HCl or H_2SO_4 are used in processes like chemical cleaning, decaling, pickling, acid oil-well acidizing, etc., suffering from severe corrosion [1-4]. Because these acids are very aggressive, industries that use them suffer from substantial economic losses due to corrosion on their metallic parts. One of the most widely methods to overcome this problem is the use some organic compounds as corrosion inhibitors [5,6]. However, the these organic inhibitors have a nature toxic and it has required research activities in recent times toward finding alternative less toxic, and more friendly with environemnt acid corrosion inhibitors [7-10]. To avoid environmental and human problems with the use of these organic compounds, natural products have been reported in previous studies and used as corrosion inhibitors for different metals in various environments [11-18].

Salvia hispanica L. (Chia) has been used in America much time before the Spanish people came. Before their arrival, the species known commonly as *"Chia"* was a major for food, medicine, and oil [19]. The fatty acids (FA) of chia oil are highly unsaturated, with their main components being linoleic and α-linolenic acids, with a chemical structure as given in Fig. 1, two polyunsaturated fatty acids impossible for human body be produced. They can be used to help to control cholesterol and triglyceride levels, blood pressure and reducing the risk of heart disease.

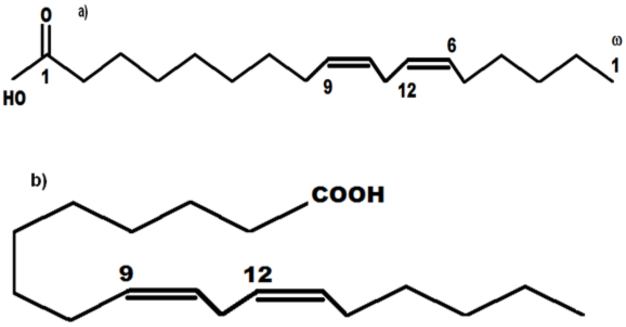


Figure 1. Chemical structure for a) Linoleic and b) α-linolenic acids.

In addition to this, it contains omega-3 fatty acids which are anti-inflammatory agents, very useful for patients with rheumatoid arthritis and lupus [20].

Different electrochemical techniques are used to evaluate inhibitors performance such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization curves and electrochemical noise (EN) measurements [21-26]. EN technique measures the spontaneous variations in current and potential with the estimation of the electrochemical noise resistance, R_n, as the ratio between standard deviation of potential, σ_v, divided by the standard deviation of current, σ_i,

$$R_n = \sigma_v / \sigma_i \qquad (1)$$

It is a very well known the fact that the noise signal gives information about the dynamics that occur on the surface of the electrode, giving about the type of corrosion that is occurring, which can be uniform or localized. Therefore, many efforts have been carried out to study the noise signal by different methods, including the fractal analysis and Hurst exponent, H, which provides very useful information in many systems where corrosion phenomena exists [27,28]. Thus, the goal of the present work is to study the performance of the methanolic extract of *Salvia hispanica* as corrosion inhibitor for carbon steel in sulfuric acid by using electrochemical techniques, making special emphasis in EN measurements to evaluate this inhibitor for short periods of time.

2. EXPERIMENTAL PROCEDURE

The testing material were 1018 carbon steel rods with a chemical composition including 0.14%C, 0.90% Mn, 0.30%S, 0.030% P and as balance Fe, encapsulated in commercial epoxic resin with an exposed area of 1.0 cm^2. Corrosive solution was 0.5 M H_2SO_4 was prepared with double distilled water. *Salvia hispanica*, Chia, seeds were obtained from a local market, soaked in methanol (approximately 250 ml of methanol per 100 g of chia) during 30 days until all methanol was evaporated obtaining a solid, which was weighed and dissolved in methanol and obtained as a stock solution and used then for preparation of the desired concentrations. Inhibitor concentrations includes 0, 100, 200, 400, 600, 800 and 1000 ppm. Techniques used in this reserch were Electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) measurements. For this, we left the specimen to reach a stable open circuit potential value, E_{corr}. A conventional electrochemical cell with three electrodes with a graphite electrode as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode was used. EIS experiments were performed at E_{corr} by using a signal with amplitude of 10 mV in a frequency interval of 100 mHz-100 KHz. For this, a model PC4 300 Gamry potentiostat was used. EN reading were taken in both current and potential noise by using two identical working electrodes and a saturated calomel reference electrode (SCE) at a sampling rate of 1 point per second in blocks of 1024 seconds during 24 hours of immersion. A zero resistance ammeter (ZRA) from ACM instruments was used in this case. Trend removal was applied by adjusting a least square fitting method. The noise resistance value, $R_{n,}$ was calculated as the ratio of potential noise standard deviation, σ_v, over current noise standard deviation, σ_i. Surface examination of the corroded electrodes was accomplished by LEO VP 1450 scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

As an example, Figs. 2 and 3 show the Nyquist curves for carbon steel in 0.5 M H_2SO_4 at 0 and 1000 ppm of *Salvia hispanica* at different immersion times. For the blank uninhibited solution, it is very clear that at the beginning of the tests, data displayed a single, capacitive, semicircle at high and intermediate frequencies with what appears to be an inductive loop at lower frequency values, indicating an adsorption-desorption controlled process. However, as time elapsed, data displayed a single capacitive-like semicircle with its center at the real axis. The semicircle diameter reached its highest value after four hours of immersion, and after that time, it decreased continuously as time elapsed, maybe because of the non-protective nature of the corrosion products. For the solution containing 1000 ppm of inhibitor, Fig. 3, data displayed a single capacitive semicircle at short testing times, indicating a charge-controlled process. For longer testing times, however, an inductive loop appeared at low frequency values, indicating an adsorption-desorption controlled process. The semicircle diameter was much higher than that obtained in the uninhibited solution, indicating the protective character of the film formed by the *Salvia hispanica*. Semicircle diameter increased as time elapsed, reaching its highest value after two hours of testing due to the growth of the protective formed external film, but it decreased with a further increase in time, reaching values lower than that obtained at the beginning of the test.

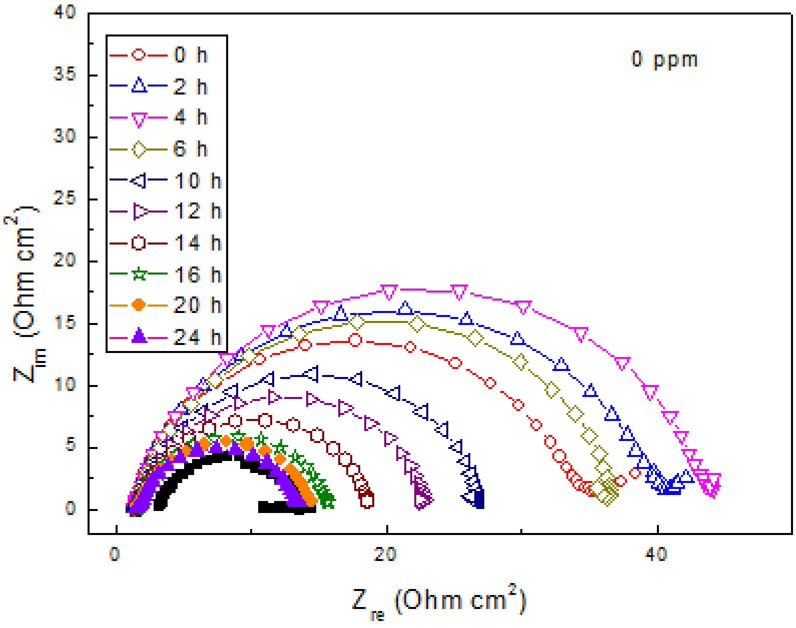


Figure 2. Nyquist curves for carbon steel in 0.5 M H_2SO_4 containing 0 ppm of *Salvia hispanica* at different exposure times.

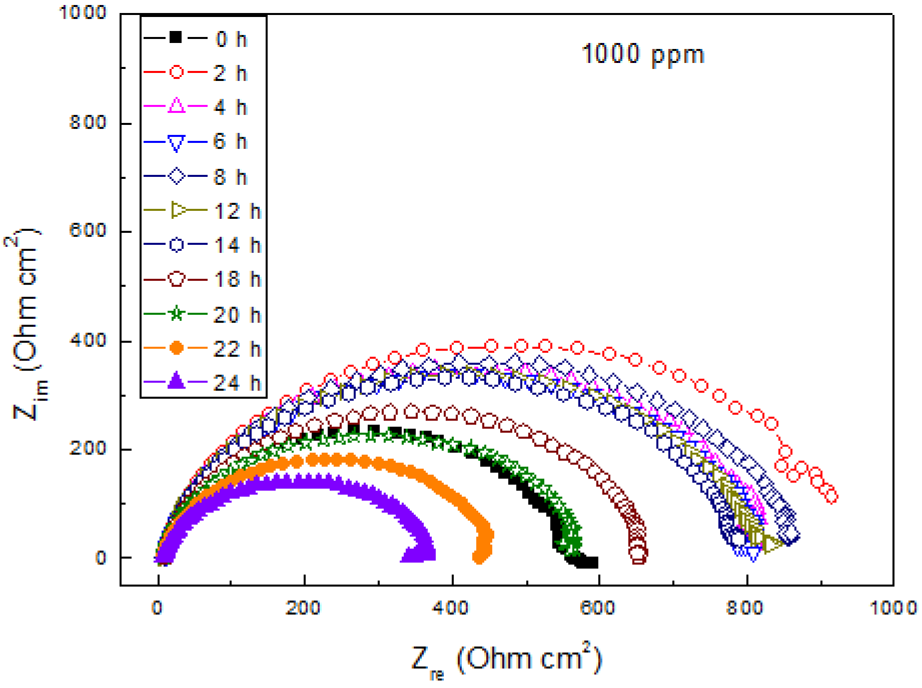


Figure 3. Nyquist curves for carbon steel in 0.5 M H_2SO_4 containing 1000 ppm of *Salvia hispanica* at different exposure times.

This decrease in the semicircle diameter suggests a decrease in the corrosion protection given by the film formed inhibitor due to its possible desorption. Calculating the polarization resistance value, R_p, which corresponds to the diameter of the semicircle, Fig. 4, for different concentrations it can be seen that the R_p value increased with the addition of *Salvia hispanica* up to 1000 ppm, thus, reducing the corrosion in the steel.

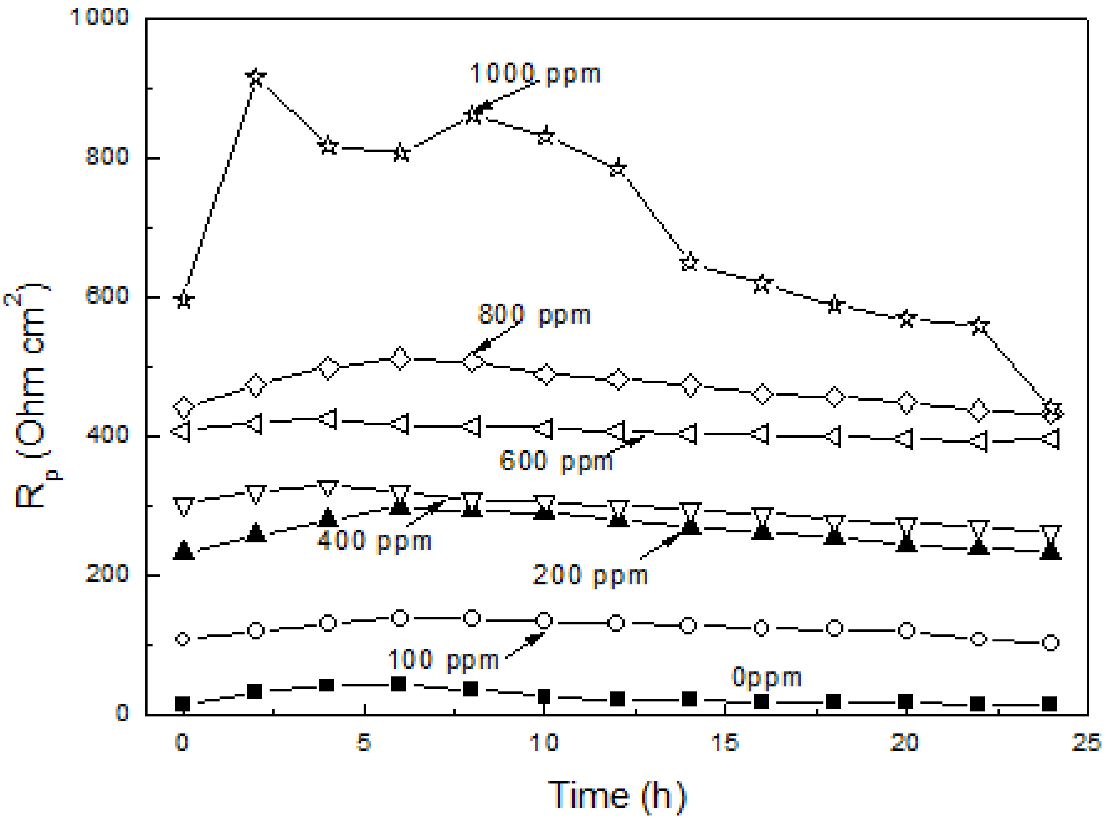
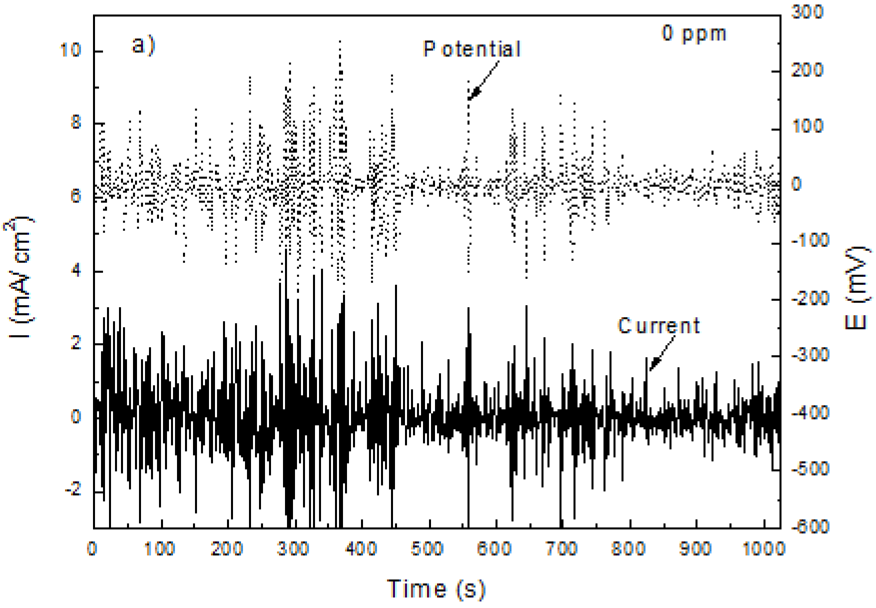


Figure 4. Variation in the R_p value with time for carbon steel in 0.5 M H_2SO_4 containing different concentrations *of Salvia hispanica* extract.



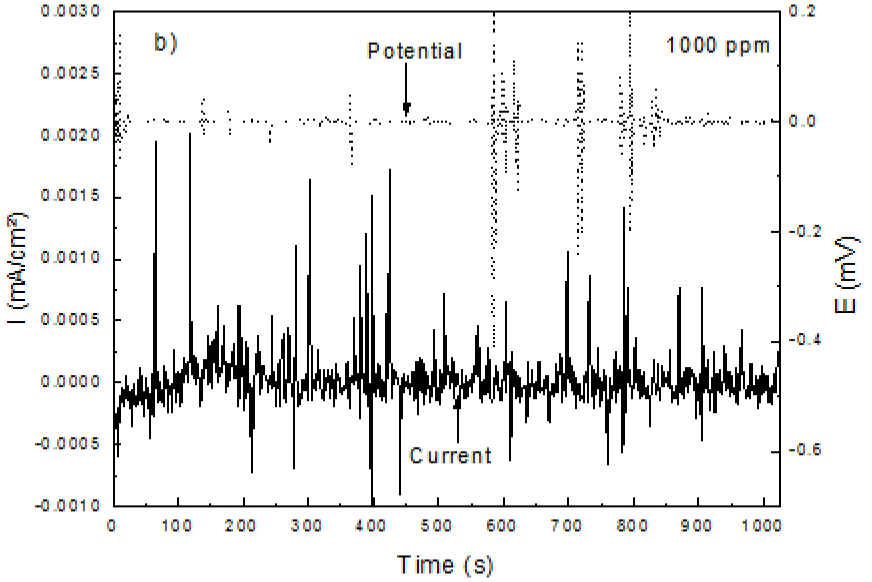


Figure 5. Noise in current and potential for carbon steel in 0.5 M H_2SO_4 containing a) 0 and b) 1000 ppm *of Salvia hispanica* extract.

Time series in both current and potential for the uninhibited solution and with 1000 ppm of *Salvia hispanica* are shown in Fig. 5. For the uninhibited solution, the observed transients correspond to a steel corroded in the whole surface, whereas those observed in the inhibited solution corresponds to a steel being attacked in very localized places [29]. This is because the inhibitor forms a protective film on the surface metal which can be disrupted in some localized places giving rise to the observed transients.

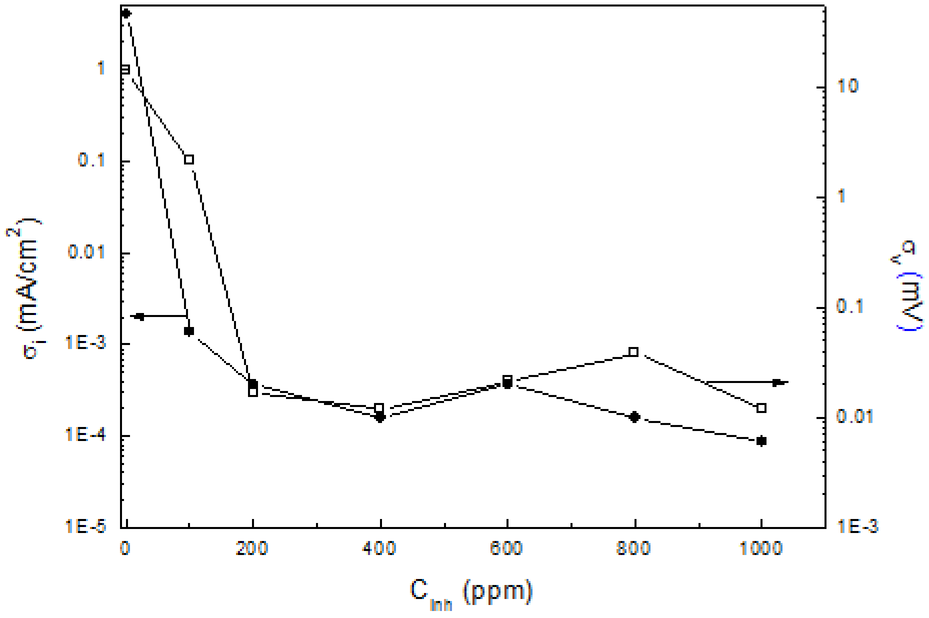


Figure 6. Effect of the *Salvia hispanica* extract concentration on the standard deviation of potential, σ_v, and standard deviation of current, $\square_i$.

It is very clear that the transients in both current and potential are reduced in intensity when the inhibitor is added to the system in more than 2 orders of magnitude, as shown in Fig. 6, where the standard deviation in potential and in current, a measure of the transients intensity, are plotted, indicating a change in the corrosion attack, either uniform or localized.

The combination of both time series in current and in potential allow us to calculate the noise resistance as given in Eq. (1), and thus, calculate the overall corrosion rate since R_n is inversely proportional to I_{corr}. The variation with time for the R_n values at the different inhibitor concentrations are shown in Fig. 7, where it can be seen that its value increased with increasing the inhibitor concentration, similar to the behavior exhibited by R_p, Fig. 4.

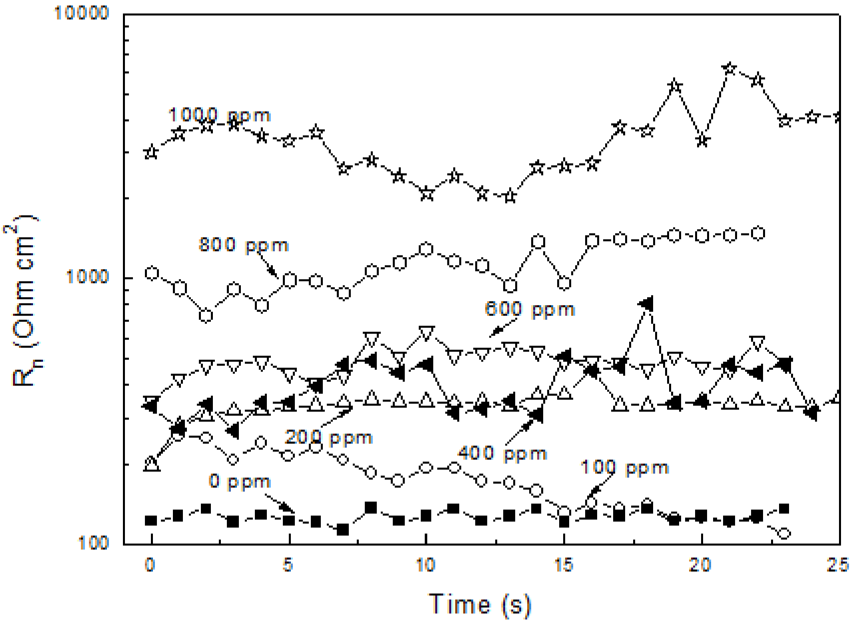


Figure 7. Variation in the R_n value with time for carbon steel in 0.5 M H_2SO_4 containing different concentrations *of Salvia hispanica* extract.

However, it must be said that the R_n values were higher than those for R_p, maybe because in the noise data there are many current and potential transients related to localized events, whereas R_p is more related to uniform corrosion events [29].

Inhibitor efficiency values (IE) were calculated by using eqs. (2) and (3)

$$IE = \left(\frac{R_{ni} - R_b}{R_{ni}}\right) x\ 100 \qquad (2)$$

$$IE = \left(\frac{R_{pi} - R_b}{R_{pi}}\right) x\ 100 \qquad (3)$$

where R_{ni} and R_{pi} are the noise and polarization resistance with inhibitor respectively, whereas R_b is the resistance without inhibitor. A comparison of the IE calculated from EIS and EN data for the best inhibitor concentration (1000 ppm) at different times of immersion is shown in Fig. 8.

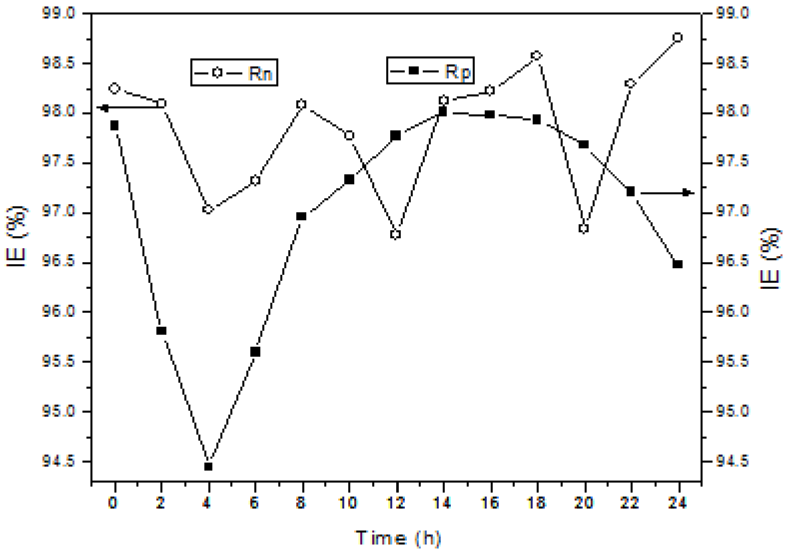


Figure 8. Change in the inhibitor efficiency value with time obtained with EN and EIS measurements.

The results clearly shown that in both cases a similar behaviour is observed with the IE value remaining above 94%. However, at 24 hours the efficiency obtained from EN increased, reflecting the sensitivity to localized attack using electrochemical noise.

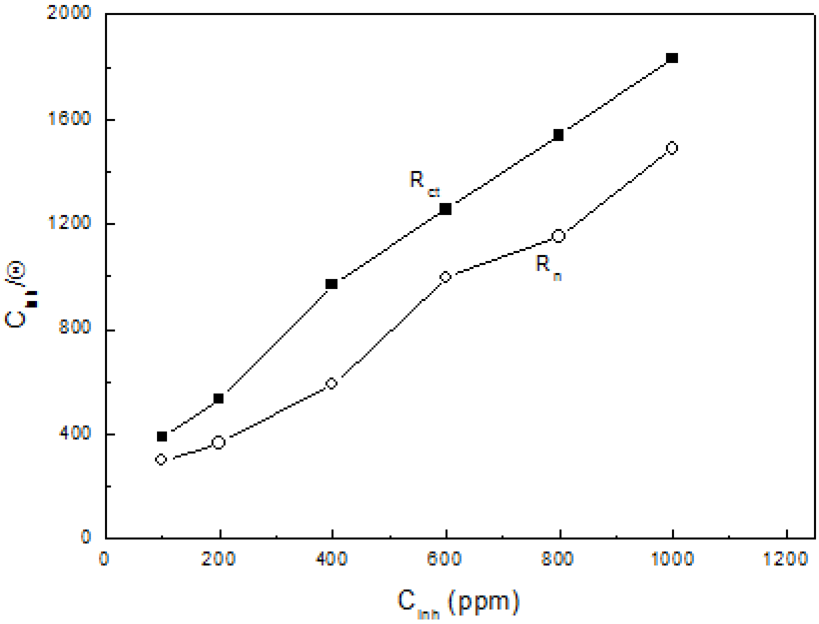


Figure 9. Langmuir adsorption plots for carbon steel in the absence and presence of different concentrations of *Salvia hispanica* extract in 0.5 M H_2SO_4.

To obtain more information on the way these compounds are adsorbed on the surface of carbon steel, Langmuir, Frumkin, Freundlich and Temkin isotherms were adjusted to the experimental data , and, as cen be seen in Fig. 9, Langmuir isotherm gave the best fit. The surface coverage (θ) is given by IE/100 and its relationschip with the inhibitor concentration (C_{inh}) can be represented by the Langmuir adsorption isotherm, the isotherm is given by [30]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (4)$$

where K_{ads} is the equilibrium constant for the adsorption-desorption process constant, C_{inh} is the concentration of the inhibitor. Results are plotted in Fig. 9, where it can be seen that the strong correlation ($R^2 > 0.90$) between the experimental data with eq. (4) indicates that the inhibitor is adsorbed of on the carbon steel surface following this isotherm. The assumption of Langmuir adsorption isotherm is that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species [31].

The Gibbs standard free energy of adsorption for the inhibitor was estimated by using following equation [21-24]:

$$\Delta G^{\circ}_{ads} = -RT\ lnK_{ads} \qquad (5)$$

and a value for K_{ads} of 5.70 was obtained, whereas for $\Delta G°_{ads}$ the calculated value was -14.22 KJ/mol, thus $\Delta G^{\circ}_{ads} < -20\ KJ \cdot mol^{-1}$ indicating a physisorption and if $\Delta G°_{ads}$ is lower than –40 KJ/mol a chemisorcion process is under control. 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.

As shown above in Fig. 2, Nyquist plots have the shape of a depressed semicircle with its centre on the real axis. The simplest equivalent electric circuit corresponds to a parallel combination of a capacitance and a resistance. To take into account the surface roughness, constant phase elements, CPE, replace the capacitor, and they are often used to a better modelling of depressed semicircles. The CPE impedance a is given by:

$$Z=Z_o(j\omega)^{-n} \qquad (6)$$

where *n* is between 0 and 1. Parameter *n* is 1 for an ideal capacitor. In real systems, the ideal capacitive behaviour is not observed due to surface roughness, heterogeneities or other effects that cause uneven current distributions over the electrode surface. The degree of heterogeneity of a surface is given when $n < 1$, [32]. If *n* value is a little bit higher than 0.5, corresponds to a severe heterogeneity, but when *n is equal* to 1, the metal surface is completely smooth. The fractal dimension of the surface is related to this degree of heterogeneity [33]. An object with complex structure is a “fractal”, providing new details at higher degrees of magnification [34, 35].

It is possible to determine the fractal dimension, i.e the roughness, of the electrode surface by considering the degree of depression of the Nyquist impedance plot by using following equation [36]:

$$n = 1/(D_{fs} - 1) \qquad (7)$$

where D_{fs} is the fractal dimension of the surface. D_{fs} can take values between 2 (for a surface completely smooth) to values close to 3 (for a rough surface).

On the other hand, the noise data can be analysed in the time domain by making use of the Hurst exponent H [37]. Mandelbrot has given mathematical equations to study the fractal geometry by [38] for the analysis and characterization of the structure and scaling exponents of fractal time records. The fractal dimension D_f describes the structure of a fractal, e.g., the “roughness” of an EN time record and provides the explanation for the values of D_f, H and β that are observed for some of the EN time series parameters, and noise spectra. By using the fractional Brownian motion (fB_m) Mandelbrot technique gives the connection between the structure of the EN time record and the spectral density function SDF (characterized by D_f, H and β) and the microscopic behaviour (oxidation reactions) responsible for corrosion if we define the fractal dimension D_f by:

$$D_f = 2 - H = (5-\beta)/2 \qquad (8)$$

The Hurst exponent H, gives a long-term time dependence in a time series which can be calcuted by analysing the oscillations present in the data. If the variation in the time record over a specific time interval (the lag time) is proportional to the lag time raised to the power H, the time series is said to be fractal. The Hurst´s rescaled range analysis based on his empirical law proposed [39, 40]:

$$R/S = (\tau / 2)^H \qquad (9)$$

where the difference between the maximum and minimum values is R, S the standard deviation of the time series, τ is the period of time measured and *H* the Hurst exponent. *H* is taken as a measure of the memory for the system, which can be related with the corrosion type. The Hurst exponent, take values between 0 and 1. When $H = 0.5$ reflects that the observations are statistically independent of each other. When H is between 0 and 0.5, it is called as anti persistence zone, i.e. phenomena with a short memory effect; if $0.5 < H < 1$, called persistence zone, it is a phenomena with large memory effect, and related to the corrosion condition. D_f is the fractal dimension of the electrochemical noise-time series and related to the surface fractal dimension obtained from EIS data (D_{fs}), which can take values closer to 1 for a straight (smooth) line, to values close to 2 for broken(rough) lines in the noise current time series [32, 40].

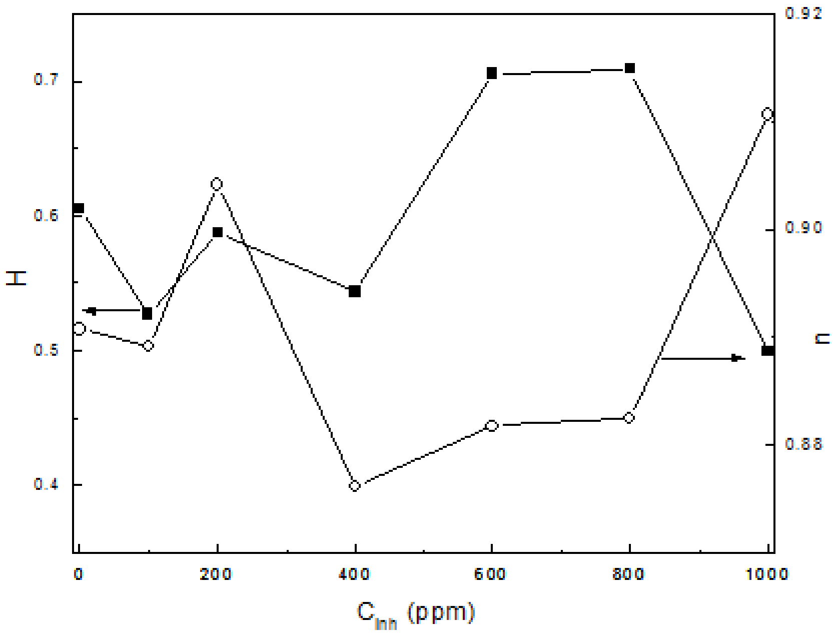


Figure 10. Effect of the *Salvia hispanica* concentration on the H and n values.

If we use EIS data, eq. (7) to calculate H and n, and we plot them versus the inhibitor concentration Fig. 10, but if we use EN data and calculate D_{fs} and D_f at different inhibitor concentrations by using eq. (8), Fig. 11, two things are worthwhile to notice: first of all, the H and *n* values calculated by using both methods of analysis gave complementary results; second although the H value for 0 ppm was higher than 0.6, Fig. 10, this value decreased to a value lower than 0.5 for a inhibitor concentration of 1000 ppm, which represent a phenomenon with a short memory effect and noisy signals associated to pitting corrosion [40]. Anti-persistent conditions are obtained for corrosion inhibition.

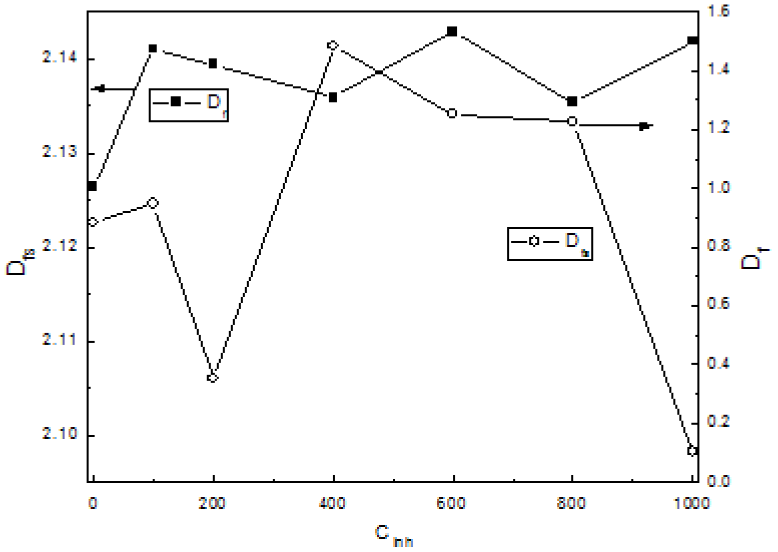


Figure 11. Variation of D_{fs} (obtained with EIS) and D_f (obtained with EN) as a function of the inhibitor concentration.

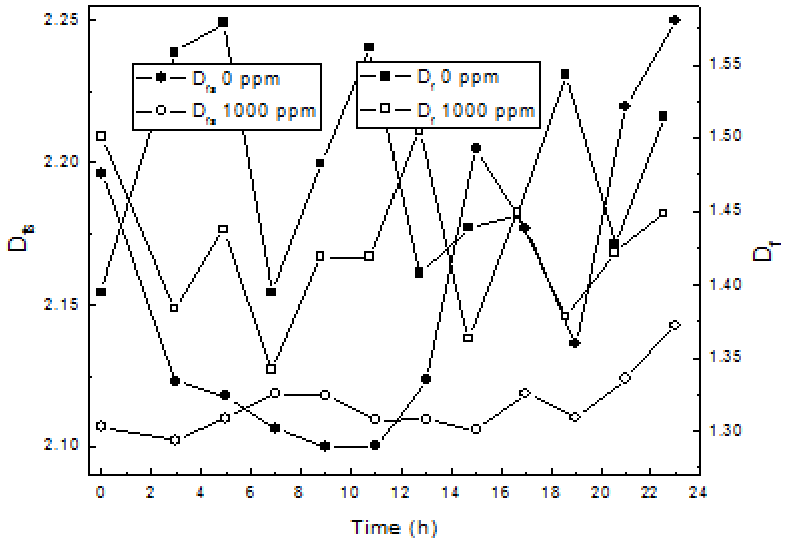


Figure 12. Variation n the D_{fs} and D_f values with time at 0 and 1000 ppm of *Salvia hispanica*.

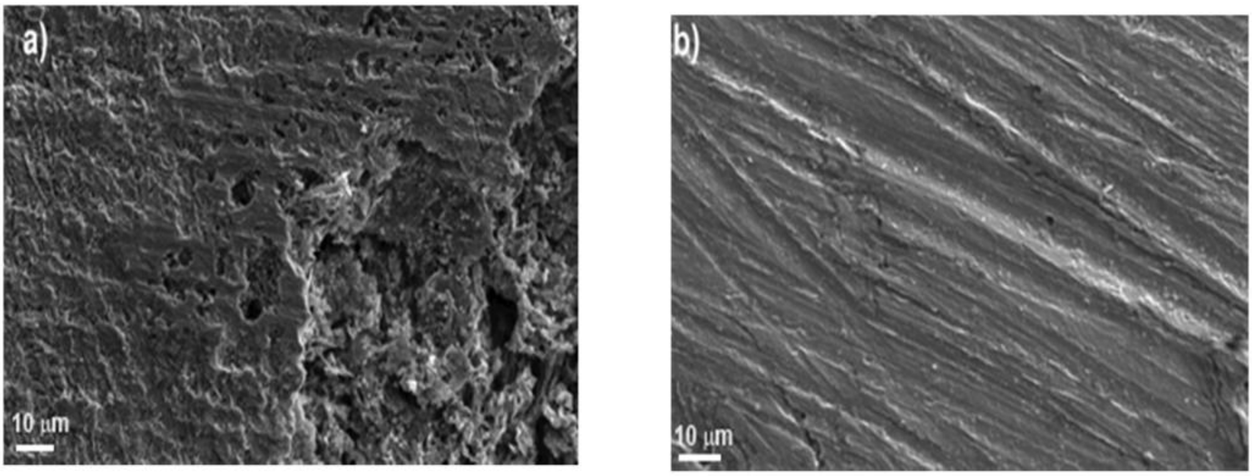


Figure 13. SEM micrograph of corroded specimen in 0.5 M H_2SO_4 solution containing a) 0 and b) 1000 ppm of *Salvia hispanica.*

This could be due to the film formation due to the corrosion process occurring in those sites, which decreases the corrosion rate, and thus giving the anti-persistent condition at high inhibitor concentration. The complementary *n* value (0.91) obtained from impedance measurements suggest for 1000 ppm inhibitor concentration, Fig. 10, a pure capacitive behavior as expected for an inhibited corrosion surface.

Fig. 11 presents the surface fractal dimension (D_{fs}) and the current noise-time series fractal dimension (D_f) as a function of inhibitor concentration, where a smoothed metal surface and constant D_f (around 1.4) values were obtained, whereas Fig. 12 presents D_{fs} and D_f as a function of immersion time for 0 and 1000 ppm of inhibitor. This figure shows that the D_{fs} value reaches a value closer to 2 with the addition of 1000 ppm of inhibitor indicating a smoother surface, but without inhibitor the values tend to increase after 12 hours of immersion, reaching a value close to 2.25, indicating a rougher metal surface due to a higher corrosion rate [32]. However in relation to the solution containing 1000 ppm of *Salvia hispanica*, the D_f values obtained from the noise current–time series for the inhibitor condition, the values obtained are lower than the ones presented without inhibitor condition suggesting a smoother surface throughout the whole testing time.Thus, both techniques, EIS and EN, gave similar results once again.

An SEM micrograph of the corroded surfaces of the steel sample after 24 hours immersion at in the 0.5 M H_2SO_4 containing 0 and 1000 ppm inhibitor can be seen in Fig. 13. It can be observed that the in the uninhibited solution, the steel surface shows a very rough appearance due to the corrosion process itself, whereas in the inhibited solution, surface is almost without attack, as predicted by the analysis done above. It becomes clear that the inhibitor acted correctly since it stopped the corrosion attack to acts over the material surface.

4. CONCLUSIONS

A study of the use of *Salvia hispanica* as a green inhibitor for 1018 carbon steel in 0.5 M H_2SO_4 has been carried out by using electrochemical impedance spectroscopy and electrochemical noise measurements. Polarization (R_p) and noise resistance (R_n), Hurst exponent and fractal dimension were calculated by using both type of measurements. *Salvia hispanica* showed to be a good inhibitor since both R_p and R_n increased more than one order of magnitude with the addition of 1000 ppm of *Salvia hispanica* due to its adsorption on the surface metal following a Langmuir adsorption isotherm. Calculation of H and D_f gave very similar results by using both EIS and EN measurements, indicating that this type of analysis is a very promising technique to evaluate inhibitors performance.

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