ETHANOL EXTRACT OF FAGUS SYLVATICA LEAVES AS AN ECO-FRIENDLY INHIBITOR FOR CARBON STEEL CORROSION IN ACIDIC SOLUTIONS

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Abstract: Carbon steel corrosion inhibition by Fagus Sylvatica leaves ethanol extract has been studied in 0.5 M H_2SO_4 solution using open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy methods of corrosion monitoring. The studies were conducted using a Voltalab 40 Radiometer Analytical potentiostat/galvanostat and VoltaMaster 4.0 for acquiring and processing the experimental data. The results of the study revealed that different concentration of Fagus Sylvatica leaves ethanol extract inhibits carbon steel corrosion. Inhibition efficiency was found to vary with concentration. From Tafel and Nyquist diagrams, one can observe that the presence of Fagus Sylvatica extract increases the polarization resistance, shift the corrosion potential towards more positive values and decreases the corrosion rate. The inhibition efficiency was calculated and the results obtained by both methods are well correlated.

Key words: Corrosion of carbon steel, Fagus Sylvatica leaves, Inhibitor

1. INTRODUCTION

The development of new corrosion inhibitors, non toxic, and not containing heavy metals and organic phosphates is a very important matter as we know from many reports on this subject [1-3]. Inorganic compounds such as chromate and nitrate are used on a large, industrial, scale as corrosion inhibitors in various environments and for different metals and alloys. [4-7]. The bio-toxicity of these compounds, especially chromates is well known, as well as they are environmental unfriendly, characteristics that narrow their use.

Among the possible corrosion inhibitors organic compounds containing one or many polar functions (with N, O and S atoms) were found to be efficient in corrosion prevention by completing the heterocyclic compounds containing polar groups and p electrons. The inhibiting effect of these organic compounds is usually considered to be due to metallic surface interaction by adsorption.

Steel and its alloys are widely used in industry and because of this their corrosion behaviour study in different aggressive media is necessary. Acid solutions are used in the most important industrial applications in etching and acid cleaning.

Among other corrosion protection methods the use of inhibitors is one of the most convenient methods of decreasing metal corrosion rates especially in acid solutions [8-11].

Over the years, considerable efforts have been made to find suitable compounds of organic origin to be used as corrosion inhibitors in various corrosive media [12-20]. The aim of this work is to study the inhibition action of Fagus Sylvatica (FS) leaves extract in different concentrations, on the corrosion behaviour of carbon steel in aerated 0.5 M H_2SO_4 solutions by using electrochemical methods potentiodynamic polarization, electrochemical impedance spectroscopy and open circuit potential.

2. EXPERIMENTAL

The working electrodes were made from carbon steel (weight %, C: 0.049, Mn: 0.227, Cr: 2.34, S: 0.0005, Fe: rest). The solutions were prepared using analytical grade reagents and double distilled water. Fagus Sylvatica (FS) plant extract was prepared at the National Institute of Chemical and Pharmaceutical Research and Development in ethanol solution (75% v/v – volume percentage) and was added in 0.5 M H_2SO_4 solution in appropriate quantities to obtain 0.05, 0.1, 0.2, 1 and 2 % volume. All experiments were made at room temperature 25 ± 1^0C in aerated solution.

A standard electrochemical 50 mL thermostated with three electrodes was used in the corrosion experiments. The working electrode was a carbon steel square with a geometric aria of 0.5 cm^2. Before each experiment the electrode surface was polished with emery paper of different grades, rinsed with distilled water and dried. The auxiliary electrode was a Radiometer Analytical platinum

electrode with the surface of 1.13 cm^2 and the reference electrode was a Radiometer Analytical saturated silver/silver chloride electrode immersed directly into the solution. All potentials in the text are referred to this reference electrode.

All the measurements were carried out using a Voltalab 40, Radiometer Analytical potentiostat/galvanostat interfaced with a computer using VoltaMaster 4.0 software for data acquisition and data processing. The test solutions were thermostated during all the experiments.

Before polarisation and EIS measurements, the working electrode was introduced in the test solution and left for 30 min to attain the open circuit potential at which the system had been stabilized. Polarization curve measurements were obtained at a scan rate of 20 mV/min starting from cathodic potential going to anodic direction. The open-circuit potential (OCP) versus time and potentiodynamic polarization curves were recorded. The OCP was measured for 30 minutes before starting the potentiodynamic polarization experiments.

Electrochemical impedance spectroscopy (EIS) was carried out at the open-circuit potentials in the frequency range 100 kHz– 50 mHz with a sinusoidal potential perturbation of 10mV amplitude. The data of impedance spectra results were fitted on equivalent circuits, a Randles type circuit, using ZView software and the impedance parameters polarization resistance R_p and double layer capacitance C_{dl} were obtained.

3. RESULTS AND DISCUSSIONS

Open circuit potential

The variation of potential in open circuit does not provide direct information regarding the corrosion kinetics. However it provides qualitative information regarding the system thermodynamics. The potentials in open circuit have been measured as a function of immersion time for carbon steel samples immersed in an aerated unstirred solution of H_2SO_4 0,5 M in the absence and in the presence of some concentrations of various Fagus Sylvatica extract at 25^{0}C the obtained results being presented in Figure 1. The measurement of open circuit potential variation versus time for the working electrode is important for the determination of corrosion fields, the partial and complete inhibition processes and for the determination of appropriate inhibition concentrations [21].
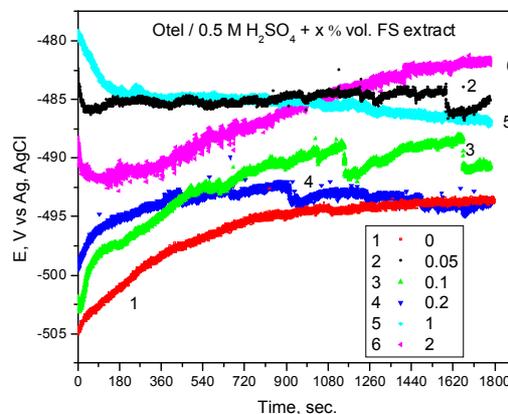
Fig. 1 Open circuit potential variation versus time for carbon steel in H$_2$SO$_4$ 0.5 M solution without and with various concentrations of FS extract, 25^{0}C

As one can see in Figure 1 the presence of plant extracts greatly influence the value of OCP for all cases tending it towards more electropositive values. These results suggest that adding the plant extracts one can obtain an inhibition of corrosion for carbon steel in sulphuric acid solution. The variation of OCP towards more electropositive values indicates the covering of metallic surfaces with products that decrease the corrosion rate.

In some cases, the OCP is shifted at the beginning towards more electronegative values and after a period of time the potential is shifted towards more electropositive values. This behaviour can be attributed to an initial dissolution process followed by the formation of a protective layer absorbed on the electrode surface.

Potentiodynamic polarization results

In Figure 2 are presented the potentiodynamic polarization curves for carbon steel in H$_2$SO$_4$ 0.5 M solution in the absence and in the presence of various concentrations of Fagus Sylvatica extract at 25^{0}C.

The electrochemical corrosion parameters: corrosion potential, E_{corr}, corrosion current density, i_{corr}, anodic and cathodic Tafel slopes, b_a and b_c, resulting from the polarization curves are presented in Table 1.

The inhibition efficiency (IE, %) was calculated with the equation [22]:

$$IE = \left(1 - \frac{i_{corr}}{i^0_{corr}}\right) \times 100, \% \qquad (1)$$

where i^0_{corr} and i_{corr} are the corrosion current densities of carbon steel electrode in 0.5 M H_2SO_4 solution without and with different concentration of Fagus Sylvatica extract respectively.
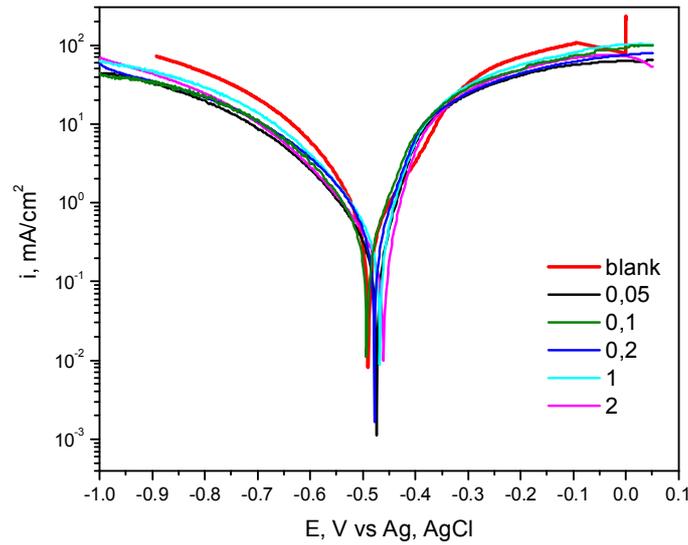
Fig. 2 Tafel plots of carbon steel immersed in 0.5 M H$_2$SO$_4$ with or without Fagus Sylvatica extract, 25^{0}C

As can be seen from the results presented in Table 2 the presence of Fagus Sylvatica extract results in the decrease of the corrosion current density, i$_{corr}$, for all the extract concentrations. Moreover, in the presence of plant extract the values of corrosion potential E$_{corr}$ are shifted, generally, towards more electropositive values compared to the value obtained in the absence of Fagus Sylvatica extract.

The corrosion current densities, as can be seen from Figure 2, slowly decrease, indicating that Fagus Sylvatica extract is acting on both anodic and cathodic reaction rates, but having a higher influence on the cathodic reaction, therefore, Fagus Sylvatica extract could be classified as a mixed-type inhibitor with predominant cathodic effectiveness.

Table 1 Kinetic parameters derived from Tafel plots of carbon steel immersed in 0.5 M H$_2$SO$_4$ with or without FS, 25^{0}C

FS conc., % vol.	i$_{corr}$, mA×cm^{-2}	E$_{corr}$, mV/Ag, AgCl	R$_p$, Ω×cm^2	-b$_c$, mV/dec	b$_a$, mV/dec	θ	IE, %
0	0.7383	-483	44.66	110	74	-	-
0.05	0.1467	-478	69.58	75	44	0.801	80.13
0.1	0.3015	-496	46.12	88	64	0.592	59.16
0.2	0.3606	-482	43.25	104	61	0.512	51.16
1	0.3362	-471	46.63	113	53	0.545	54.46
2	0.2072	-465	72.42	113	44	0.719	71.93

The anodic and cathodic Tafel slopes (Table 1), b$_a$ and b$_c$, have a small change, indicating that the inhibiting action occurred by simply blocking the available anodic and cathodic active areas on the metal surface.

The calculated inhibition efficiencies show that a good inhibition action of Fagus Sylvatica is obtained at the highest studied concentration but also for the lowest one. The anodic Tafel slopes, b$_a$ slowly decreases in the solution with FS extract showing small changes in steel corrosion mechanism.

The degree of surface coverage θ of the metal surface is calculated using the equation [23]:

$$\theta = 1 - \frac{i_{corr}}{i_{corr}^0}$$

(2)

where i$_{corr}^0$ and i$_{corr}$ are the corrosion current densities in the absence and in the presence of inhibitor, respectively. The degree of surface coverage (Table 1) shows a uniform adsorption of plant extract on the metal surface.

Electrochemical impedance spectroscopy

The corrosion behaviour of carbon steel in 0.5 M H$_2$SO$_4$ solution in the presence of Fagus Sylvatica extract was investigated by electrochemical impedance spectroscopy at 25^{0}C after 30 minutes of immersion.

Figure 3 shows the results of EIS experiments in the Nyquist representation at the respective open circuit potentials.

After analyzing the shape of Nyquist plots it is concluded that the curves are formed by a single capacitive semicircles, showing that the corrosion process was mainly charge transfer controlled [24, 25]. The general shape of the curves is very similar throughout the whole concentrations, indicating that almost no change in the corrosion mechanism occurred due to the inhibition action. The diameter of Nyquist plots increases with addition of Fagus Sylvatica extract.
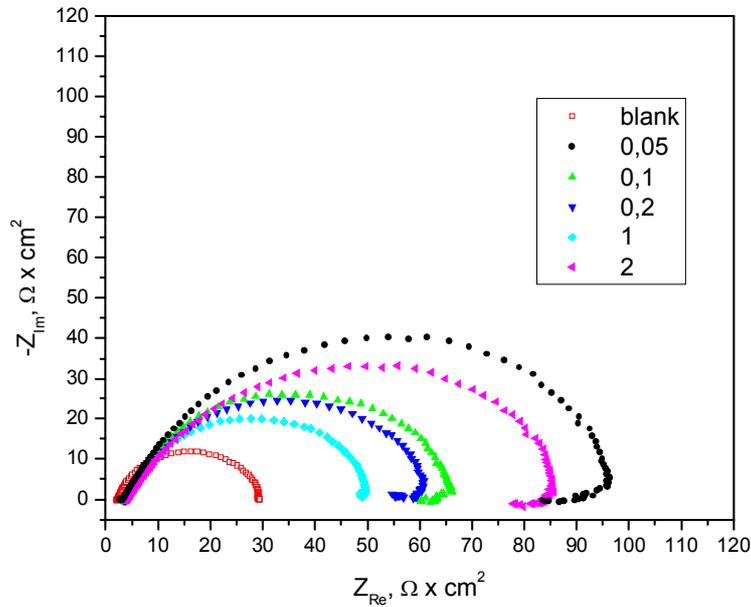
Fig. 3 Impedance plots of carbon steel immersed in 0.5 M H_2SO_4 with or without FS, 25^0C

It is clear from Figure 3 that the semicircles obtained are depressed. This behaviour can be attributed to electrode surface state and frequency dispersion effects [24, 26].

Various electrochemical parameters derived from Nyquist plots are calculated and listed in Table 2. The values of R_p were given by subtracting the high frequency impedance from the low frequency one, as follows:

$$R_p = Z_{Re}(\text{at low frequency}) - Z_{Re}(\text{at high frequency})$$
$$(3)$$

where Z_{Re} is the real component of the impedance.

A high value of polarization resistance indicates an increased corrosion resistance.

The values of electrochemical double layer capacitance C_{dl} were calculated at the frequency f_{max}, at which the imaginary component of the impedance is maximal ($-Z_{max}$) by the following equation [23]:

$$C_{dl} = \frac{1}{2\pi f_{max} R_p} \qquad (4)$$

The values of percentage inhibition efficiency (IE, %) were calculated from the values of R_p according to the following equation [27]:

$$IE, \% = \left(1 - \frac{R_p}{R_p^0}\right) \times 100$$
$$(5)$$

where R_p and R_p^0 are the values of the polarization resistance in the absence and in the presence of the inhibitor respectively.

The impedance data listed in Table 2 indicate that the values of R_p and IE, % increase while the values of C_{dl} are found to decrease in the presence of inhibitor. The behaviour can be attributed to a decrease in dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the inhibitiro molecules act by adsorption mechanism at carbon steel/acid interface [28]. Bode plots are shown in Figure 4. The plots indicate the presence of one time constant corresponding to one depressed semicircle that was obtained in case of Nyquist plots. The highest inhibition efficiency value was obtained at the lowest Fagus Sylvatica concentration (0.05%).
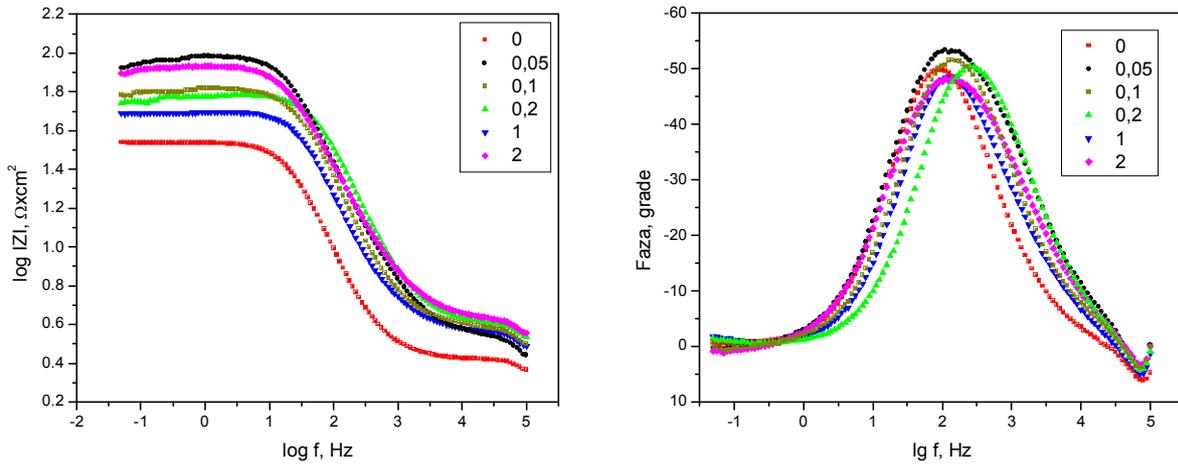
Fig. 4 Bode plots for steel in 0.5 M H$_2$SO$_4$ solution with various Fagus Sylvatica concentrations 25^{0}C

The thickness of the protective layer increases with increase in inhibitor concentration since more molecules will adsorb electrostatically on the electrode surface. This process can give a noticeable decrease of C$_{dl}$, a trend that is in accordance with Helmholtz model given by the equation [28]:

$$C_{dl} = \frac{\varepsilon_r \cdot \varepsilon_0 \cdot A}{d} \qquad (6)$$

where d is the thickness of the protective layer, ε_r is the dielectric relative constant of the medium, ε_0 is the vacuum permitivity and A is the effective surface aria of the electrode. The C$_{dl}$ value is always smaller in the presence of the inhibitor than in the absence as a result of the effective adsorption of the inhibitor.

By knowing the above described parameters one may now calculate the thickness of the protective layer and hence to compare the effectiveness of each individual inhibitor [29].

Table 2 The impedance parameters and the percent of protection efficiency for steel in 0.5 M H$_2$SO$_4$ solution containing different concentration of Fagus Sylvatica 25^{0}C

FS conc. % vol.	R$_p$, Ω×cm^2	C$_{dl}$, µF cm^{-2}	φ$_{max}$, degree	IE, %
0	24.79	130.5	-50	-
0.05	81.25	79.77	-53	69.47
0.1	58.23	80.44	-52	57.43
0.2	53.54	43.29	-50	53.7
1	57.77	91.30	-49	57.09
2	70.05	90.38	-48	64.61

For comparison, the variation of the values of percentage inhibition efficiency (IE, %) with the inhibitor concentration obtained from potentiodynamic polarization and EIS technique are shown in Figure 5.
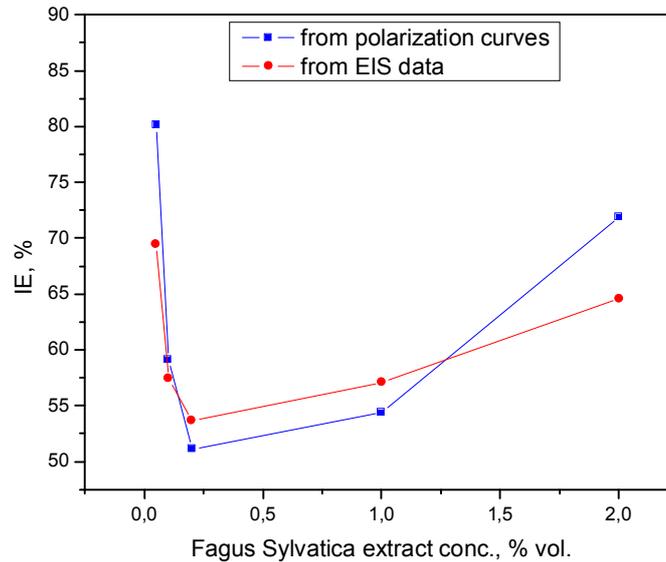
Fig. 5 Relationship between inhibition efficiency IE, and Fagus Sylvatica extract concentration for steel in 0.5 M H$_2$SO$_4$, 25^{0}C

It can be observed that the best inhibition efficiencies were obtained for 0.05 and 2 % vol. Fagus Sylvatica concentrations. The results indicate good agreement between the values of corrosion efficiency as obtained from the impedance technique and polarization measurements. It can be concluded that the corrosion rate depends on the chemical nature of the electrolyte rather than the applied technique.

The Nyquist plots were analyzed by fitting the experimental data to a simple equivalent circuit model, Figure 6, that include the solution resistance, R$_s$ and the constant phase element (CPE) which is placed in parallel to polarization resistance element R$_p$. The R$_p$ value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate.
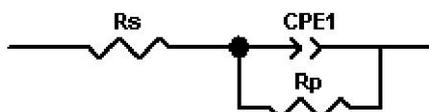
Fig. 6 Proposed equivalent electrical circuit for steel interface in 0.5 M H$_2$SO$_4$ solution without and with Fagus Sylvatica extract

The electrode impedance, Z, in this case is represented by the mathematical equation [27]:

$$Z = R_s + \left[\frac{R_p}{1 + (2 \cdot \pi \cdot f \cdot R_p \cdot C_{dl})^\alpha} \right] \qquad (7)$$

were α denotes an empirical parameter, $0 \leq \alpha \leq 1$.

To compensate for non-homogeneity in the system, the capacitance was implemented as a constant phase element (CPE) that is defined by two values, T and n. The impedance, Z, of CPE is presented by equation [27]:

$$Z_{CPE} = T^{-1}(j\omega)^{-n} \qquad (8)$$

were ω is the angular frequency in rad$\times$s^{-1}, $\omega = 2\pi f$ and f is the frequency in Hz. If n equals 1 then Z_{CPE} is identical to that of a capacitor $Z_C = (j\omega C)^{-1}$ were C is the capacitance. In fact a capacitor is actually a constant phase element with a constant phase angle of 90^0. For a non-homogeneous system, n values ranges from 0.9 to 1. The capacitance of the double layer (C$_{dl}$) is calculated from equation (4), where f$_{max}$ is the frequency at the maximum height of the semicircle on the imaginary axis.

Table 3 Electrochemical fitting parameters of steel in 0.5 M H$_2$SO$_4$ in the absence and in the presence different concentration of Fagus Sylvatica extract

Fagus Sylvatica concentration, % vol.	R$_s$, $\Omega \times$cm^2	CPE1-T μF/cm^2	CPE1-P	R$_p$, $\Omega \times$cm^2
0	2.42	244.2	0.89	27.2
0.05	3.371	199.71	0.79	101.1
0.1	3.816	170.83	0.85	61.84
0.2	4.008	100.14	0.86	56.39
1	3.676	222.78	0.84	46.95
2	4.188	221.25	0.79	83.22

The reaction parameters calculated from fitting the impedance results with the proposed equivalent circuit are presented in Table 3. The equivalent circuit was chosen as to obtain the best correlation between the experimental and the fitting data [30-32]. An example of the experimental data and the fitted curve are shown in Figure 6. The correlation obtained, as can be seen, is very good.
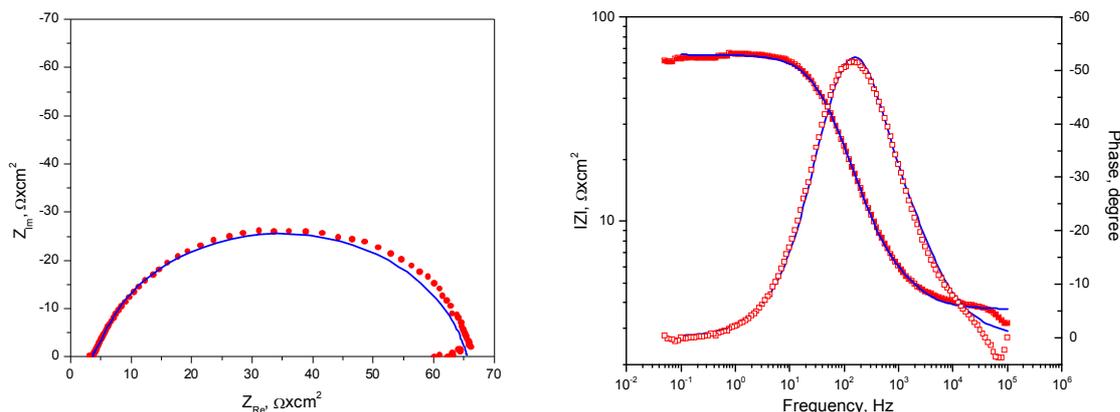
Fig. 6 Example of the Nyquist and Bode plots for steel interface in 0.5 M H$_2$SO$_4$ solution with 0.1% vol. Fagus Sylvatica extract, 25^{0}C. Scattered points are the experimental data and solid lines show the model fit

The polarization resistance is increasing in the presence of Fagus Sylvatica extract, increase associated with a decrease of a double layer capacitance C$_{dl}$. The lowest concentration of Fagus Sylvatica correspond to the highest value of the polarization resistance.

4. CONCLUSIONS

In this paper the inhibition effect of Fagus Sylvatica ethanol extract on the corrosion behavior of carbon steel in 0.5 M H$_2$SO$_4$ solution was investigated using the potentiodynamic polarization and electrochemical impedance spectroscopy methods. The results have showed that the studied plant extract has an inhibition effect on steel in sulphuric acid solution the best efficiencies being obtained for the 0.05% vol. Fagus Sylvatica concentration.

The open circuit potential variation versus time shows that an addition of the above mentioned plant extract shifts the OCP towards more electropositive values, suggesting that the studied plant extract can act as an inhibitor for the studied system.

From the polarization studies the results showed that the Tafel slopes, anodic and cathodic are both changed in the presence of Fagus Sylvatica indicating that the inhibiting action occurred by blocking the available anodic and cathodic active areas on the metal surface.

The higher inhibition efficiencies obtained were 80.13% in the presence of 0.05% vol. Fagus Sylvatica extract.

The electrochemical impedance spectroscopy measurements presented curves with a similar shape for the whole Fagus Sylvatica concentration range, formed by single capacitive semicircles, showing that the corrosion process was mainly charge transfer controlled. The diameter of Nyquist plots increases with addition of Fagus Sylvatica extract. The results obtained by both electrochemical methods are in good agreement.

The EIS results were analyzed by fitting the experimental data to a simple equivalent circuit model. The R$_p$ value, a measure of electron transfer across the surface and is inversely proportional to corrosion rate has the highest value with the addition of 0.05% vol. Fagus Sylvatica extract.

Results showed that ethanol extract of Fagus Sylvatica leaves has good inhibition properties on the corrosion of carbon steel in aerated 0.5 M sulphuric acid solution at 25^{0}C.

Acknowledgements

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