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Effect of Flowing Conditions on the Corrosion Inhibition of Carbon Steel by Extract of Buddleia Perfoliata

R. Lopes-Sesenes[1], *G.F. Dominguez-Patiño*[2], *J.G. Gonzalez-Rodriguez*[1], *J. Uruchurtu-Chavarin*[1]

[1] Universidad Autonoma del Estado de Morelos, CIICAP, Av. Universidad 1001, 62209-Cuernavaca, Mor.,Mexico
[2] Universidad Autonoma del Estado de Morelos, Facultad de Ciencias Biologicas, Av. Universidad 1001, 62209-Cuernavaca, Mor.,Mexico
*E-mail: ggonzalez@uaem.mx

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Buddleia perfoliata leaves extract has been investigated as a carbon steel corrosion inhibitor in 0.5 M sulfuric acid by using polarization curves, electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) at different rotation speeds (0, 250, 500, 1000, and 2000 ppm). Results have shown that for uninhibited conditions, the corrosion rate increases as the rotation speed increased up to 500 rpm, and then decreased with a further increase in the rotation speed; for inhibited solution, corrosion rate was lowest under static conditions and it increased with a further increase in the rotation speed. It was found that inhibitor remains on the metal surface for a few hours, but as the rotation speed increased, it was detached from the surface leaving active sites, increasing with this the susceptibilility towards localysed type of corrosion.

Keywords: Corrosin inhibitor; Buddleia perfoliata; rotation speed; electrochemical impedance**.**

1. INTRODUCTION

Organic compounds containing heteroatoms are commonly used to reduce the corrosion attack on steel in acidic media. These compounds adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion process [3-8]. The toxic nature of these organic inhibitors has required research activities in recent times toward finding alternative environmentally friendly acid corrosion. inhibitors. The so-called “green inhibitors” are organic compounds that act by adsorption on the metal surface such as ascorbic acid, succinic acid, tryptamine, caffeine, etc... [1-23]. Additionally, some other natural products such as black pepper, Azadirachta indica, Gossipium hirsutum, guanadine, Occimum viridis, Talferia occidentalis and Hibiscus sabdariffa, have been used. For instance, Oguzie carried out the inhibitive action of leaves extracts of Sansevieria trifasciata on aluminium corrosion in

2 M HCl and 2 M KOH solutions by using the gasometric technique [2]. Results indicated that the extract acted as a good inhibitor in both environments and inhibition efficiency increased with increasing the inhibitor concentration. Synergistic effects increased the inhibition efficiency in presence of halide additives. Temperature studies revealed a decrease in the inhibitor efficiency with a rise in the temperature and the corrosion activation energies increased in the presence of the extract. A mechanism of physical adsorption was proposed for the inhibition behaviour. The adsorption characteristics of the inhibitor were approximated by Freundlich isotherm. In another work by Chauhan et al. [3] the inhibition effect of Zenthoxylum alatum plant extract on the corrosion of mild steel in 5 and 15% aqueous hydrochloric acid solution has been investigated by weight loss and electrochemical impedance spectroscopy (EIS). The corrosion inhibition efficiency increased by increasing the plant extract concentration till 2400 ppm. The effect of temperature on the corrosion behaviour of mild steel in 5 and 15% HCl with addition of plant extract was studied in the temperature range 50-80 °C. Surface analysis (SEM, XPS and FT-IR) was also carried out to establish the corrosion inhibitive property of this plant extract in HCl solution. Plant extract was able to reduce the corrosion of steel more effectively in 5% HCl than in 15% HCl. The adsorption of this plant extract on the mild steel surface followed the Langmuir adsorption isotherm. Okafor et al.[4] studied the inhibitive action of leaves, seeds and a combination of leaves and seeds extracts of Phyllanthus amarus on mild steel corrosion in HCl and H_2SO_4 solutions by using weight loss and gasometric techniques. Results indicated that the extracts acted as a good inhibitor in both environments and inhibition efficiency increased with extracts concentration. Temperature studies revealed an increase in inhibition efficiency with rising the temperature; activation energies decreased in the presence of the extract. A mechanism of chemical adsorption of the plants components on the surface of the metal was proposed for the inhibition behaviour. The adsorption characteristics of the inhibitor were approximated by a Temkin type of isotherm. The corrosion efficiency of these extracts is normally ascribed to the presence, in their composition, of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as their acid hydrolysis products.

The genus Buddleia, included in the family Loganiaceae, and previously classified in a family of its own, the Buddlejaceae, is now classified in the family Scrophulariaceae. Native to Asia, Africa, North and South America, Buddleia is a genus containing 100 species, 50 being distributed in America, of which 16 grow in Mexico [22]. Buddleia species are widespread and share some remarkable similarities in their medicinal uses. This may well indicate the presence of the same or similar compounds with a particular pharmacological action. A patterns is emerging about the composition of these compounds; flavonoid and iridoid glycosids being the major seccondary metabolites that have been isolated to date [23]. Buddleia perfoliata became officialy recognized in the 1930 Mexican Pharmacopoeia where it was shown to have antisudorific activity [24]. This plant also contains essential oil, tannic, gallic and oxalic acids [25]. In folk medicin, it is used in the treatment for tuberculosis as well as for catarrh, ptyalism and headaches [25].

Usually, inhibitor efficiency increases with an increase in the inhibitor concentration until a steady state is reached. However, some inhibitors may exhibit the peak-value-phenomenon of inhibitor concentration [26, 27]. The concentration where the lowest corrosion rate is exhibited is called optimum concentration. Currently, research works on the optimum concentration of inhibitor exist in literature [26, 27] mainly for static conditions but very few works on this matter exist for flowing conditions. Bommersbach et al. [27] studied the inhibitor efficiency of a carboxylic acid and a tertiary amine on the corrosion of SAE 1038 carbon steel in a mixture of Na_2SO_4+Na_2CO_3+NaCl at different rotation speeds (0, 1600 and 3200 rpm) by using EIS measurements. They found that inhibitor film formation depends on the electrode rotation rate: film forms faster under high rotation speeds. Ochoa et al. [28, 29] studied the inhibition mechanism of carbon steel by a non-toxic multi-component inhibitor by using EIS measurements, and found that the properties of the protective formed layers on the metal surface depend on the electrode rotation rate. Finally, Ortega-Toledo et al. [30] carried out a study on the effect of flow conditions on the performance of a carboxyethyl-imidazoline as CO_2-corrosion inhibitor for API X-120 pipeline at 0, 250, 500, 1000 and 2500 rpm, and found that for the uninhibited solution, corrosion rate increased with an increase in the rotation speed, but for the inhibited solution, the lowest corrosion rate was obtained at 500 rpm, and it increased at lower or higher rotation speeds. In the present paper, the inhibitory effect of Buddleia perfoliata in the corrosion of 1018 carbon steel in 0.5M H_2SO_4 at different rotation speeds by using and electrochemical techniques was evaluated.

2. EXPERIMENTAL PROCEDURE

Corrosion tests were performed on coupons prepared from 1018 carbon steel rods containg 0.14% C, 0.90% Mn, 0.30% S, 0.030% P and as balance Fe. The aggressive solution, 0.5 M H_2SO_4 was prepared by dilution of analytical grade H_2SO_4 with double distilled water. Cylindrical specimens 10 mm long with a diameter of 6 mm were machined and embedded in PTFE exposing an effective surface area of 0.28 cm^2 to the electrolyte. This system was machined to form the rotating disk electrode, which was ground up to 2400 grade emery paper, rinsed with distilled water, acetone, and dried under an air flow. Rotation speeds included 0, 250, 500, 1000 and 2000 rpm. Dried Buddleia perfoliata leaves (38.7 g) were soaked in 300 ml of methanol during 24 h and refluxed during 5 h obtaining a solid, wich was weighted and dissolved in methanol untill this was completely evaporated and used as a stock solution and used then for preparation of the desired concentrations by dilution. Tests were performed by adding 100 ppm of inhibitor. Electrochemical techniques employed included potentiodynamic polarization curves, electrochemical impedance spectroscopy, EIS, and electrochemical noise, EN, measurements. In all experiments, the carbon steel electrode was allowed to reach a stable open circuit potential value, E_{corr}. Polarization curves were recorded by triplicate 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 Lugging capillary bridge. Corrosion current density values, I_{corr}, were obtained by using Tafel extrapolation. EIS tests were carried by triplicate out at E_{corr} by using a signal with amplitude of 10 mV in a frequency interval of 100 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. Finally, electrochemical noise measurements were carried out by recording current fluctuations by applying a potential of 750 mV_{Sce} at a sampling rate of 1 point per second for a period of 1024 seconds. A fully automated zero resistance ammeter (ZRA) from ACM instruments was used in this case. Removal of the DC trend from the raw noise data was the first step in the noise analysis. To accomplish this, a least square fitting method was used.

3. RESULTS AND DISCUSSION

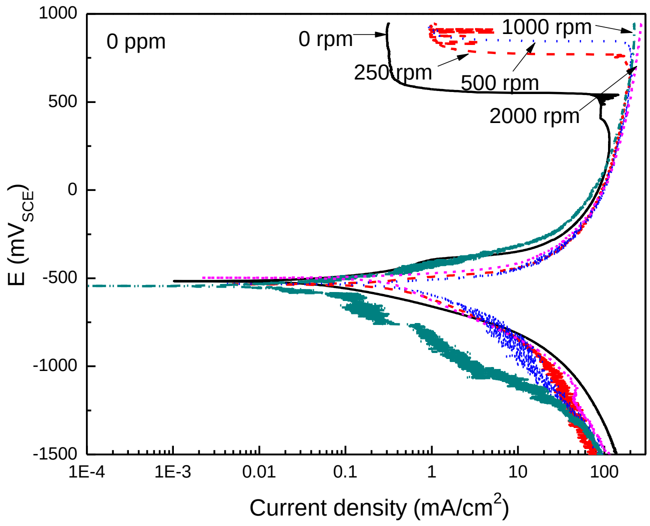

Figure 1. Effect of rotation speed in the polarization curves for carbon steel in uninhibited 0.5 M H_2SO_4 solution.

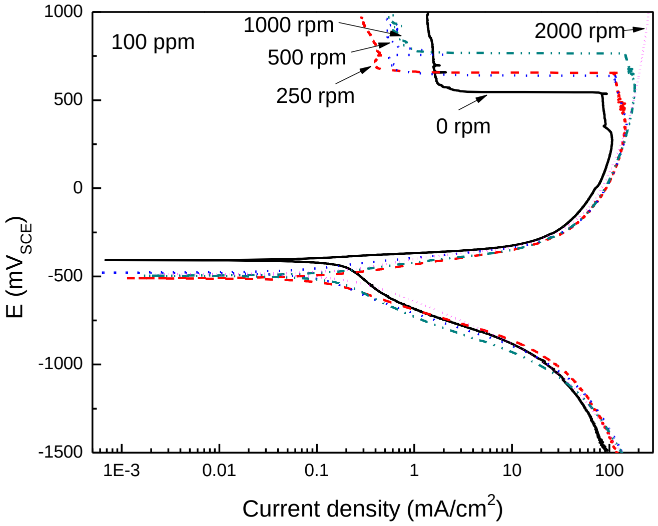

Figure 2. Effect of rotation speed in the polarization curves for carbon steel in 0.5 M H_2SO_4 solution containing 100 ppm of Buddleia perfoliata leaves extract

The effect of rotation speed in the polarization curves for carbon steel in uninhibited 0.5M H_2SO_4 solution is shown in Fig. 1. For static conditions, polarization curve shows an active-passive behavior with an E_{corr} value around -520 mV_{SCE} and an I_{corr} value close to 0.18 mA/cm^2. The passive region started in a passivation potential value, E_{pas}, of 630 mV_{SCE} with a passive current density value, I_{pas}, equal to 0.36 mA/cm^2. As soon as the rotation speed started to increase, the E_{corr} value became more active reaching a value of -535 mV_{SCE} at 500 rpm, it increased slightly at 1000 rpm and with a further increase in the rotation speed of 2000 rpm it reached a value of -540 mV_{SCE}. The I_{corr} value increased also with the increase in the rotation speed, reaching the highest value at 500 rpm, but it decreased with a further increase in the speed rotation. For the inhibited solution, Fig. 2, there was a marginal difference in the polarization curves at the different rotation speeds. Thus, at stagnant conditions, the noblest E_{corr} value, -410 mV_{SCE} and an I_{corr} value close to 0.2 mA/cm^2 were obtained. As soon as the rotation speed increased, the E_{corr} value became more active and remained more or less constant around -500 mV_{SCE}, but the I_{corr} value decreased slightly obtaining the lowest value at 500 rpm, but it increases again with a further increase in the rotating speed, just like for the uninhibited solution.

Table 1. Effect of the rotation speed on the electrochemical parameters for carbon steel in 0.5 M H_2SO_4 with and without Buddleia perfoliata leaves extract.

Rotation speed (rpm)	0 ppm				100 ppm			
	E_{corr} (mV)	I_{corr} (mA/cm^2)	E_{pas} (mV)	I_{pas} (mA/cm^2)	E_{corr} (mV)	I_{corr} (mA/cm^2)	E_{pas} (mV)	I_{pas} (mA/cm^2)
0	-520	0.18	630	0.36	-410	0.21	610	1.6
250	-530	0.45	865	1.00	-510	0.15	710	0.34
500	-535	0.70	955	0.9	-480	0.12	690	0.6
1000	-500	0.17	----	----	-500	0.15	820	0.8
2000	-540	0.3	----	----	-490	0.22	----	----

Table 1 shows the electrochemical parameters obtained from these polarization curves. This table shows that for the uninhibited solution, the E_{pas} value reached its lowest value for static conditions and it increased as the rotation speed increased up to 500 rpm; for higher rotation speeds, the polarization curves did not show a passive region. The passive I_{pas} value increased also with the rotation speed up to 500 rpm, but at higher rotation speeds there was no passive region. On the other hand, for the inhibited solution, the E_{pas} value reaches its lowest value under static conditions, similar to the observed behavior for the uninhibited solution, and increases by increasing the rotation speed. The I_{pas} value, dislike to that observed for uninhibited solution, decreased with an increase in the rotation speed. When compared at the same rotation speed, it can be seen that at static conditions, both I_{corr} and I_{pas} values increased when the inhibitor was added; however, when the solution was stirred, these values were lowered with the presence of inhibitor regarding of the rotation speed value, or even more, a passive behavior was induced at 1000 rpm. Thus, we can say that the presence of Buddleia perfoliata leaves extract improves the passive film properties suchs as the E_{pas} and I_{pas} values for the steel.

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:

$$Inh_{sol} + xH_2O_{ads} \rightarrow Inh_{ads} + xH_2O_{sol} \qquad [1]$$

The inhibitor may then combine with freshly generated Fe^{2+} ions on steel surface, forming metal inhibitor complexes [31, 32]:

$$Fe \rightarrow Fe^{2+} + 2e \qquad [2]$$

$$Fe^{2+} + Inh_{ads} \rightarrow [Fe\text{-}Inh]_{ads}^{2+} \qquad [3]$$

The resulting complex, depending on its relative solubility, can either inhibit or catalyze further metal dissolution. In a previous work [33] it was shown that the presence of the presence of some flavonoids as well as some essential oil, tannic, gallic and oxalic acid in the Buddleia perfoliata and in particular the formation of a complex formed with Fe^{2+} ions present in condensed tannins were the responsible to give the corrosion protection to the metal. At low concentrations the amount of inhibitor is not enough to form a compact complex with metal ions, so that the resulting adsorbed intermediate will be readily soluble in the acidic environment. But at relatively higher inhibitor concentrations, more inhibitor molecules become available for the complex formation, which subsequently diminishes the solubility of the surface layer, leading to improve the inhibition of metal corrosion, because under flow conditions there are different effects on the inhibition performance:

i) Flow can increase mass transport of inhibitor molecules that causes more inhibitor presence at metal surface. This effect can improve the inhibitor performance [34].

ii) Hydrodynamic conditions can increase mass transport of metal ions (Fe^{2+}) produced during metal dissolution from the electrode surface to the bulk solution and hence lead to less $[Fe\text{-}Inh]^{2+}$ complex presence on the electrode; this is a harmful effect for inhibition performance.

iii) The high shear stress resulted from high flow velocity can also separate the layer of adsorbed $[Fe\text{-}Inh]^{2+}$ complex and cause more desorption from the metal surface, which acts as a negative factor on the inhibitor efficiency [35]. The balance of the above mentioned effects lead to changes on inhibitor efficiency with rotation rate.

Nyquist and Bode plots for the uninhibited solution at the different rotation speeds are shown on Fig. 3. It can be seen that EIS data show depressed, capacitive-like semicircles, with their centers 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. Although the difference in the semicircles diameter was marginal, it can be seen that the lowest value, and thus the highest corrosion rate, was obtained under static conditions and at 1000 rpm, whereas the highest diameter, and thus the lowest corrosion rate, was obtained at 250 rpm. Bode diagrams, Fig. 3 b, shows that the impedance modulus has its lowest value at 0 rpm but the highest value was obtained at 250 rpm. Bode-phase diagram shows only a single peak at 100 Hz, which is shifted towards higher frequency values. The presence of only one peak shows that there is no formation of a protective layer.

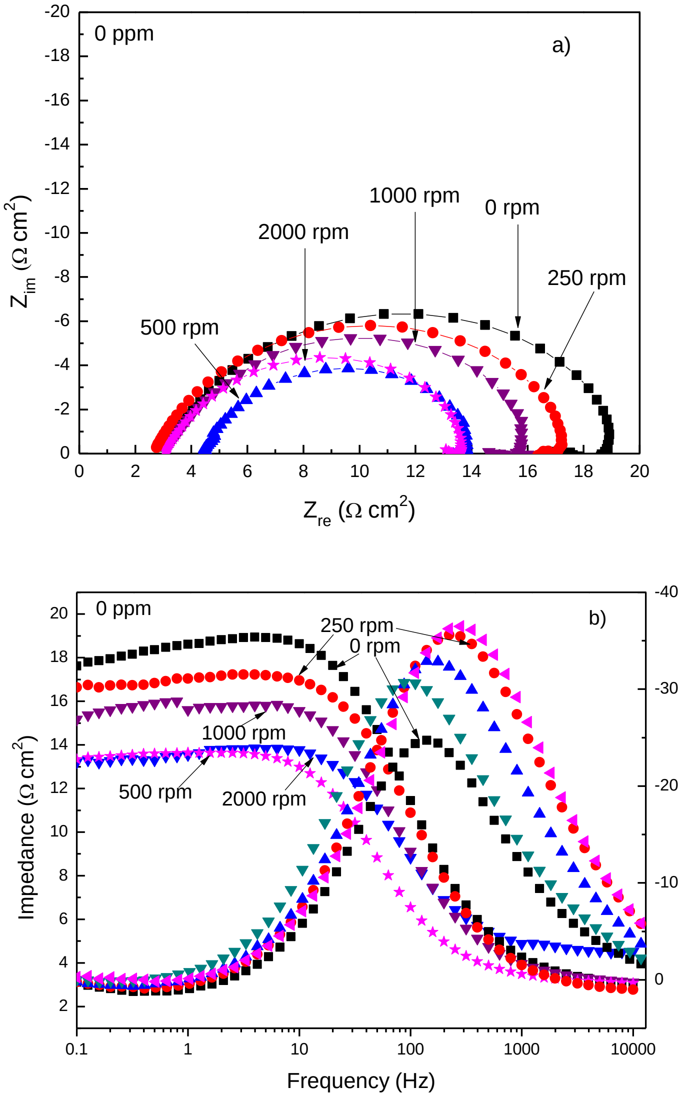

Figure 3. Effect of rotation speed in the a) Nyquist and b) Bode diagrams for carbon steel in uninhibited 0.5 M H_2SO_4 solution.

For inhibited solution, Fig. 4 a, Nyquist data describes depressed semicircles with their centers in the real axis, indicating that the corrosion process is under charge transfer from the metal to the electrolyte through the double electrochemical layer. The biggest semicircle diameter, and thus the lowest corrosion rate, is obtained under static conditions, but it rapidly decreases as the rotation speed increases, indicating an increase in the corrosion rate with the increase in the rotation speed. It should be noticed that the semicircle diameter for inhibited solution was around 25 times bigger than that obtained in the uninhibited solution, indicating a reduction in the corrosion rate by at least 25 times. Bode diagrams. Fig. 4 b, shows a single peak around 1000 Hz and it remains constant with the increase in the rotation speed. In this case is clear the harmful effect of the hydrodynamic conditions on the inhibitor performance, since an increase in the rotation speed increases the corrosion rate, which shows that high velocity flow can separate the layer of adsorbed $[Fe\text{-}Inh]^{2+}$ complex and cause more desorption from the metal surface.

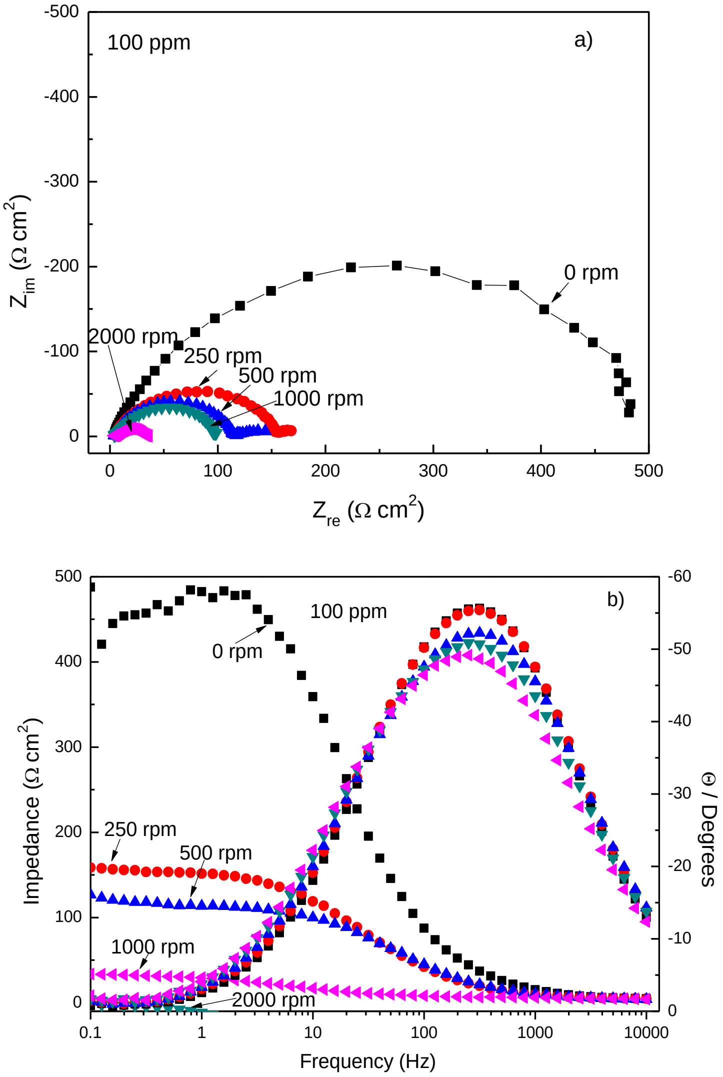

Figure 4. Effect of rotation speed in the a) Nyquist and b) Bode diagrams for carbon steel in 0.5 M H_2SO_4 solution containing 100 ppm of Buddleia perfoliata leaves extract

In order to have an insight on the film stability on the steel surface, EIS measurements were carried out during 24 h at the different rotation speeds, and Fig. 5 shows the Nyquist diagrams for the solution containing 100 ppm of inhibitor under static conditions. It can be seen that in all cases the data described depressed, capacitive-like semicircles with their centers in the real axis. At the beginning of the test (0 h) the semicircle diameter had a value which increased with time and reached its highest value after approximately 5 h of testing. After this time, the semicircle diameter decreased in a slow fashion during the first 10 h and more rapidly with a further increase in time. The semicircle diameter represents the charge transfer resistance, R_{ct}, which is inversely proportional to the corrosion rate in terms of corrosion current density, I_{corr}.

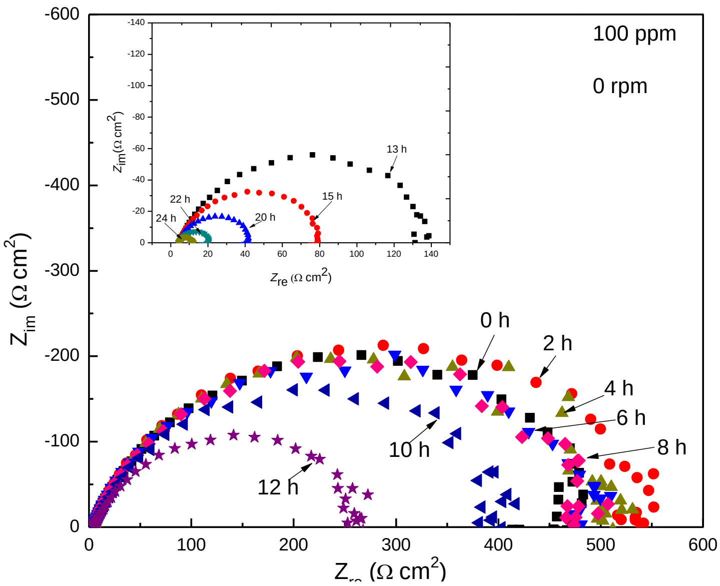

Figure 5. Change of the Nyquist digrams with time for carbon steel in 0.5 M H_2SO_4 solution containing 100 ppm of Buddleia perfoliata leaves extract at static conditions

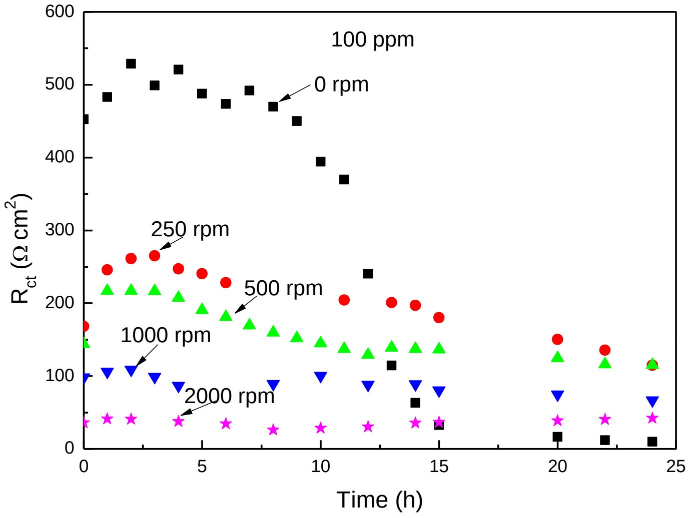

Figure 6. Change in the R_{ct} value with time for carbon steel in 0.5 M H_2SO_4 solution containing 100 ppm of Buddleia perfoliata leaves extract at different rotation speeds.

The change in the R_{ct} value with time at the different rotation speeds are shown in Fig. 6, where it can be seen that in all cases, except for the highest rotation speed (2000 rpm), the R_{ct} value increased during the first hours, but it decreased with a further increase in the testing time. This indicates that the corrosion rate decreased during the first hours and it increased as time elapses, which means that any protective film formed by the inhibitor lasts only a few hours and it is detached from the metal surface by the flow as time elapses.

The double layer capacitance, C_{dl}, was calculated from the equation bellow:

$$C_{dl} = 1/2\pi f_{max} R_{ct} \quad [4]$$

where f_{max} is the frequency value at which the imaginary component of the impedance is maximal. For the uninhibited solution, a C_{dl} value of 530 μF/cm^2 was found.

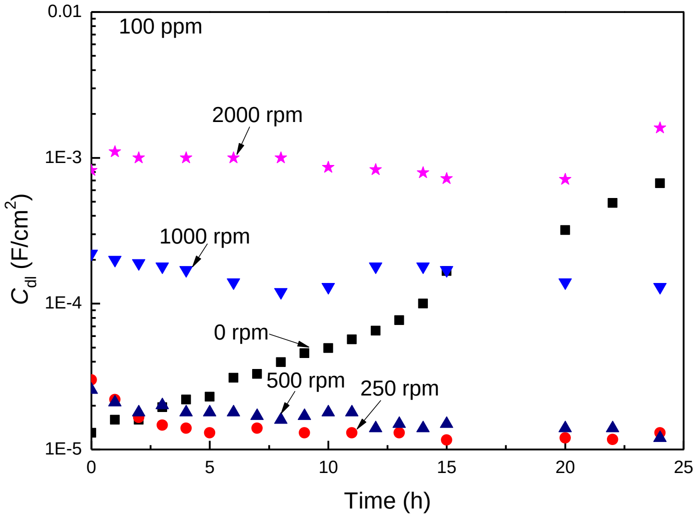

Figure 7. Change in the C_{dl} value with time for carbon steel in 0.5 M H_2SO_4 solution containing 100 ppm of Buddleia perfoliata leaves extract at different rotation speeds.

For inhibited solution under static conditions, Fig. 7, the C_{dl} value startd at 13 μF/cm^2 but it increased as time elapsed, reaching a value of 6 700 μF cm^{-2} at the end of the test. As soon as the rotation speed increased, the C_{dl} value increased reaching its highest value at the highest rotation speed. The decrease in the C_{dl} value can be interpreted as due to the adsorption of the inhibitor onto the electrode surface [36]. The double layer formed at the metal-solution interface is considered as an electric capacitor, whose capacitance decreases due to the displacement of water molecules and other ions originally adsorbed on the electrode by the inhibitor molecules, forming a protective film. The thickness of the film formed increases with increasing concentration of the inhibitor, since more inhibitor adsorbs on the surface, resulting in lower C_{dl} values. Thus, an increase in the C_{dl} value at 0 rpm as time elapses indicates a desorption of the inhibitor from the metal surface and therefore an increase in the corrosion rate.

Since the biggest effect of the inhibitor has been to improve the passive film properties such as E_{pas} and I_{pas}, some potentiostatic readings were taken by applying a potential within the passive region, in this case 750 mV_{SCE}, and the change in the current density with time was taken, Fig. 8. At static conditions, the current density decreases very fast and it reaches a more or less constant value of 1 mA/cm^2 with a transient after 600 s, where a sudden increase in the current density and a slow decay can be seen, which can be due to a breakdown and re-healing of the passive film, giving place to a localized type of corrosion such as pitting.

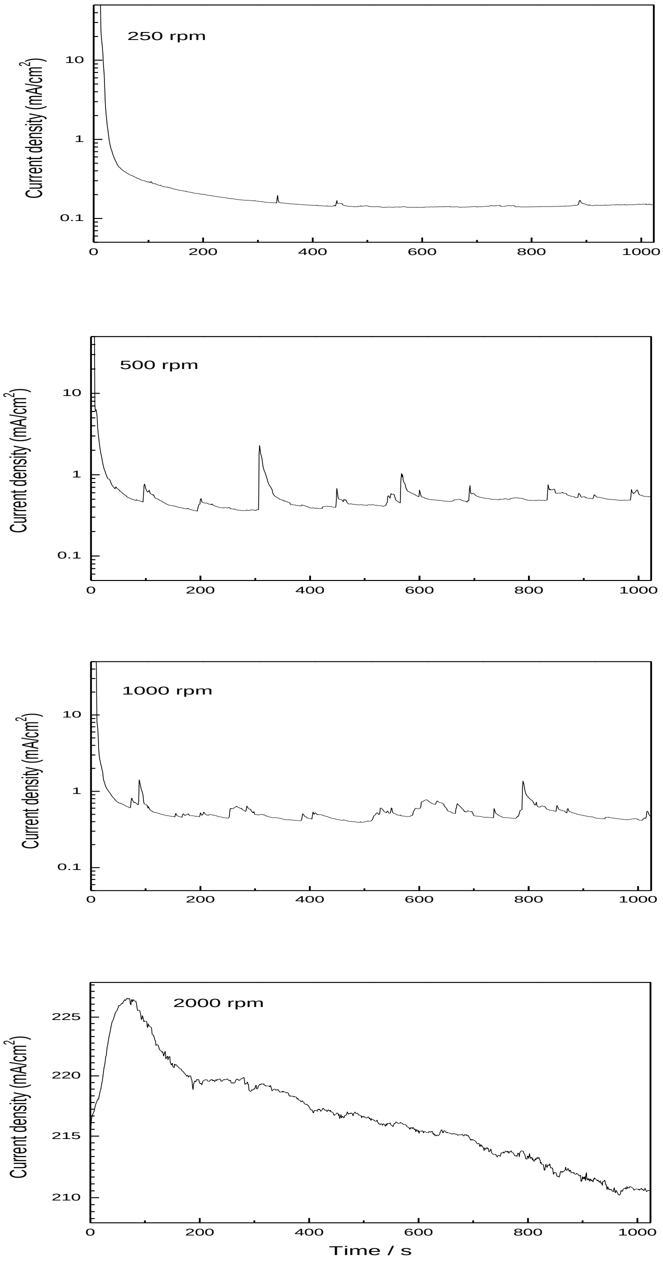

Figure 8. Noise in current for carbon steel polarized at 750 mV in 0.5 M H_2SO_4 solution containing 100 ppm of Buddleia perfoliata leaves extract at different rotation speeds.

This behavior was kept with increasing the rotation speed up to 1000 rpm, but the number of transients and, in some cases in the current density intensity, increased by increasing the rotation speed, indicating a higher number of film breakdown/re-healing events. However, at 2000 rpm, both the frequency and intensity of these transients increased, indicating that under these conditions any film-formed inhibitor did not exist anymore, leaving the metal without protection and an increase in the corrosion rate exists.

4. CONCLUSIONS

A study of the effect of Buddleia perfoliata leaves extract as corrosion inhibitor for 1018 carbon steel in 0.5 M H_2SO_4 has been investigated by using electrochemical techniques at different rotation speeds. Results have shown that inhibitor improves the passive film properties, i.e. E_{pas} and I_{pas}, except under static conditions, and its addition indeced a passive bahavior for the steel. Additionally, for the solution without inhibitor, corrosion rate increased with increasing the rotation speed up to 500 rpm, and then it decreased with a further increase in the rotation speed; on the other hand, for inhibited solution, the corrosion rate had its lowest value under static conditions and it increased with a further increase in the rotation speed. The film-formed inhibitor remained on the steel surface only a few hours, but it was detached from the steel surface with an increase in the rotation speed, leaving uncovered sites, inducing a localyzed type fo corrosion.

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