Using *Hibiscus Sabdariffa* as Corrosin Inhibitor for Al in 0.5 M H₂SO₄

L.B. Molina-Ocampo[1], M.G. Valladares-Cisneros[2], J.G. Gonzalez-Rodriguez[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 Auimicas e Ing., Av. Universidad 1001, 62209-Cuernavaca, Mor.,Mexico
*E-mail: ggonzalez@uaem.mx

The use of *Hibiscus sabdariffa* as a green corrosion inhibitor for pure Al in 0.5 M H₂SO₄ has been evaluated by using gravimetric tests and electrochemical techniques. Electrochemical techniques included potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements at 25, 40 and 60^0C whereas concentrations included 0, 200, 500, 1000, 1500 and 2000 ppm. It was found that *Hibiscus sabdariffa* is a good inhibitor for pure Al, with its efficiency increasing with the inhibitor concentration and decreasing with the temperature. *Hibiscus sabdariffa* acted as a mixed type of inhibitor, being physically absorbed onto the metal surface according to a Langmuir type of adsorption isotherm. Additionally, the inhibitive capacity of *Hibiscus sabdariffa* was due to the presence of compounds such as flavonoids with presence of lone pairs from heteroatoms and π-orbitals, blocking the active sites, decreasing, thus, the corrosion rate.

1. INTRODUCTION

The variety of applications of aluminum continues increasing due to its attractive properties such as its lightweight, strength, recyclability, corrosion resistance, durability, ductility, formability, and conductivity. Its high corrosion resistance is due to the formation of an oxide which is spontaneously formed when it is exposed to the air in the atmosphere or to aqueous solutions, oxide that protects the metal from further oxidation or corrosion. However, in aggressive media, this passivating layer can be destroyed, and corrosive attack can take place [1-4]. Many efforts have been

done by several workers to avoid Al corrosion by using organic or inorganic compounds as corrosion inhibitors to avoid this oxide dissolution [5-10].

Recently, a big interest for the use of naturally-occurring inhibitors extracted from plants has been emerged. For instance, Fares [11] evaluated the use of promising green eco-friendly pectin natural polymer as successful corrosion inhibitor on the surface of aluminum in acidic media. The inhibition efficiency first increased linearly up to 2.0 g/L, and then it increased exponentially until it reached a plateau. The maximum inhibition efficiency obtained at 10 ^{0}C using pectin concentration = 8.0 g/L was 91%, whereas at 40 ^{0}C it severely declined to 31%. Additionally, Abiola [12] evaluated the corrosion inhibition properties of *Gossypium hirsutum* L. leave extracts and seed extracts in 2 M sodium hydroxide solutions and found that *Gossypium* extracts inhibited the corrosion of aluminum in NaOH solution. The inhibition efficiency increased with increasing concentration of the extracts. The leave extract was found to be more effective than the seed extract. The leave extract gave 97% inhibition efficiency while the seed extract gave 94% at the highest concentration. In another work [13] Halambek studied the influence of (30%, v/v) ethanolic solution of Laurus nobilis L. oil on the corrosion inhibition of aluminium and AA5754 aluminum alloy in 3% NaCl solution by weight loss method, potentiodynamic polarization, and linear polarization method. The polarization measurements showed that addition of this oil in concentrations ranging from 10 ppm to 50 ppm induced a decrease of cathodic currents densities. The results confirmed that AA5754 alloy had better corrosion resistance in 3% NaCl

solution than pure aluminum, while the oil investigated had a better inhibition action on corrosion process of pure aluminum. The surface analysis via SEM techniques indicated that the active molecules from L. nobilis L. oil absolutely retarded the pitting corrosion on the specimen surfaces.

Hibiscus sabdariffa L. or roselle is used in jams, jellies, sauces and wines. The young leaves and tender stem are eaten raw in salads and chutney. The compositions contained in the flowers of *Hibiscus* species are polyphenolic acids, flavonoids, and anthocyanins [14]. Many medicinal applications of this plant have been developed around the world. For example, in China it is used to treat hypertension, pyrexia, liver damage and leukaemia due to its high content of protocatechuic acid [15]. Studies by Muhammad [16] have shown that roselle can prevent cancer, lower blood pressure and improve the digestive system in humans. Its calyx extract has also been used as an effective treatment for patients with kidney stones due to its uricosuric effect [17]. In addition to having the above mentioned activities, roselle extract can also perform as an antioxidant. For example, it protects against low density lipoprotein (LDL)-oxidation and has hypolipidemic effects in vivo [18,19]. Thus, the goal of the present work is to evaluate the use of *Hibiscus sabdariffa* as a potential green corrosion inhibitor for Al in acid media.

2. EXPERIMENTAL PROCEDURE

Hibiscus sabdariffa petals were obtained from a local market. They were crushed, and 10 g were soaked in 50 mL of boiling 1.0 M H_2SO_4 during 3 h, filtered and left until all the acid has been

evaporated and used as stock soluiton. From the stock solution, inhibitor test solutions were prepared in the concentration range 200–2000 ppm using excess acid as solvent.

Material evaluated in this work was pure, commercial aluminum rods obtained from a local store, encapsulated in commercial epoxic resin with an exposed area of 1.0 cm^2. Weight loss experiments were carried out with Al rods 2.5 cm length and 0.6 cm diameter abraded with fine emery paper until 1200 grade, rinsed with acetone, and exposed to the aggressive solution during 72 h. After this time, specimens were taken out, washed with distilled water, degreased with acetone, dried and weighed accurately. Tests were performed by triplicate at room temperature (25 °C), 40 and 60 °C by using a hot plate. Corrosion rates, in terms of weight loss measurements, ΔW, were calculated as follows:

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

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

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

were ΔW_1 is the weight loss without inhibitor, and ΔW_2 the weight loss with inhibitor. Specimens were removed, rinsed in water and in acetone, dried in warm air and stored in a dissicator. Specimens were weighed in an analytical balance with a precision of 0.1 mg. Electrochemical techniques employed included potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements, EIS. In all experiments, the carbon steel electrode was allowed to reach a stable open circuit potential value, E_{corr}. Polarization curves were recorded at a constant sweep rate of 1 mV s^{-1} at the interval from -500 to +500 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. Electrochemical impedance spectroscopy tests were carried 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.

3. RESULTS AND DISCUSSION

The effect of *Hibiscus sabdariffa* concentration on the weight loss for pure Al at 25, 40 and 60^{0}C is shown in Fig. 1, where it can be seen that, at the same temperature, the weight loss decreases with increasing the inhibitor concentration, reaching the lowest value with the addition of 2000 ppm of *Hibiscus sabdariffa*. Similarly, the weight loss increases with increasing the temperature, which might

be due to inhibitor degradation with the temperature. Inhibitor efficiency increased with an increase in the inhibitor concentration, Fig. 2, obtaining a highest efficiency value of 88 % at 25^0C, which indicates that the decrease in the corrosion rate is due to the inhibitor adsorption on the steel surface. In order to have a better insight on the way that *Hibiscus sabdariffa* molecules are absorbed on to the steel surface, different absorption isotherms were tested, including Langmuir, Frumkin, Freundlich and Temkin isotherms.
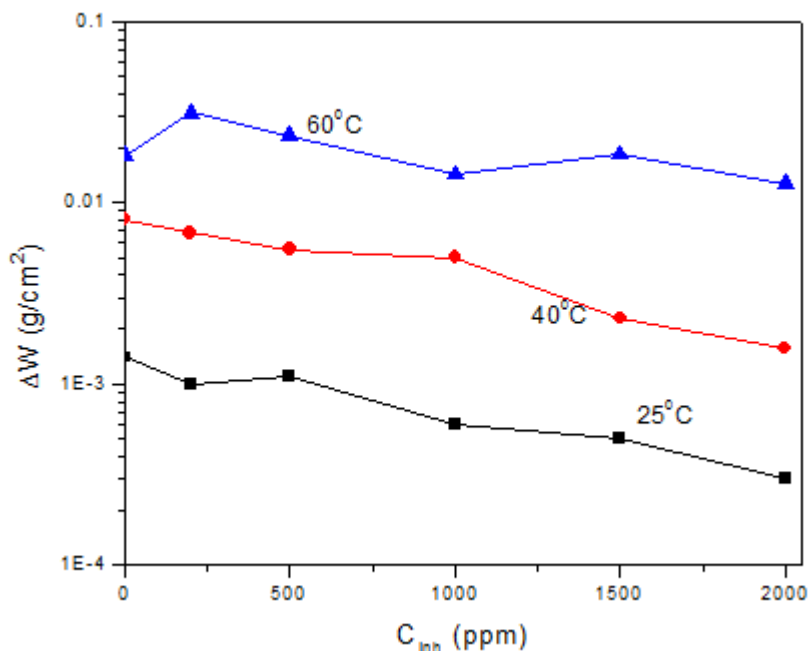
Figure 1. Effect of *Hibiscus sabdariffa* concentration on the weight loss for pure Al in 0.5 M H_2SO_4 at 25, 40 and 60^0C.
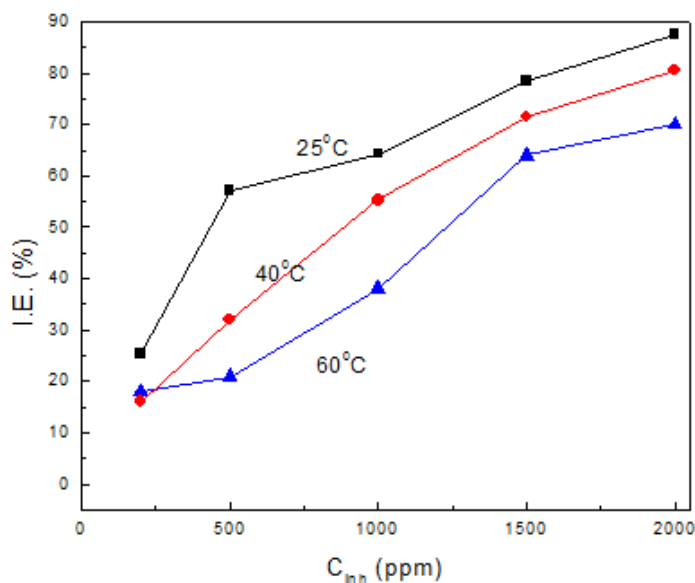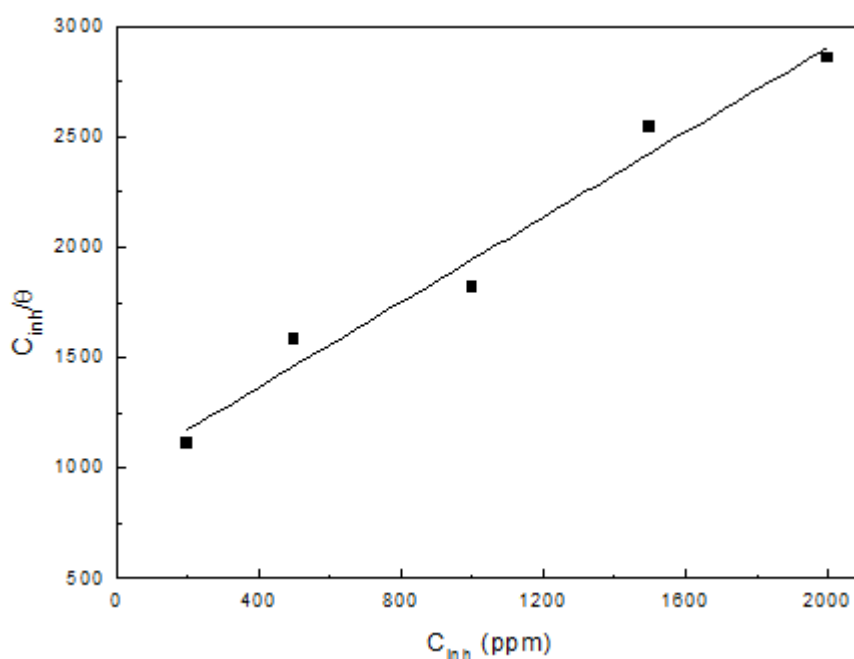

Figure 2. Effect of *Hibiscus sabdariffa* concentration and testing temperature on the inhibitor efficiency for pure Al in 0.5 M H_2SO_4.

However, the best fit was obtained from the Langmuir isotherm. Correlation between surface coverage (θ) defined by IE/100 and the inhibitor concentration (C_{inh}) can be represented by the Langmuir adsorption isotherm, the isotherm is given by [20]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad [3]$$

where K_{ads} is the equilibrium constant for the adsorption-desorption process constant, C_{inh} is the concentration of the inhibitor and (θ) the surface coverage values obtained from the weight loss tests. Langmuir adsorption isotherm assumes that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species [21]. The results are plotted in Fig. 3, the strong correlation ($R^2 > 0.90$) between the experimental data with eq. [3] suggests that the adsorption of inhibitor on the carbon steel surface obeyed this isotherm.

Figure 3. Langmuir adsorption plots for pure Al in the absence and presence of different concentrations of *Hibiscus sabdariffa* extract in 0.5 M H_2SO_4.

The K_{ads} value may be taken as a measure of the strength of the adsorption forces between the inhibitor molecules and the metal surface [22]. Large values of K_{ads} imply more efficient adsorption and hence better inhibition efficiency [23].

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

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

The equilibrium constant K_{ads} of ΔG, in the present study, is relatively high, 3.09, when compared with other studies of a good inhibitors in acidic medium for corrosion of steel [25], implies

that more *Hibiscus sabdariffa* was adsorbed onto carbon steel surface leading to great surface coverage and protection efficiency. Generally, values of ΔG up to -20 kJ mol^{-1} are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption) while those more negative than -40 kJ mol^{-1} involves charge sharing or transfer from the inhibitor components to the metal surface to form a coordinate type of bond (which indicates chemisorption) [26]. In the present study, the value of ΔG is -23.75 kJ mol^{-1} indicates that the adsorption of *Hibiscus sabdariffa* on carbon steel surface involves physical adsorption. Physical adsorption is a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. From the different compounds found in *Hibiscus sabdariffa* [27] (thiamine, niacin, ascorbic acid, and anthocyanins), positively charged species (thiamine and anthocyanins) is expected to adsorb under electrostatic attraction with the negatively charged Al surface giving rise to physical adsorption mechanism. Adsorption of negatively charged species is facilitated if the metal is positively charged. Positively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions adsorbed on the metal surface [28, 29]

Table 1. Electrochemical parameters obtained from the polarization curves.

| C_{inh} (ppm)	E_{corr} (mV)	I_{corr} (mA/cm^2)	β_a (mV/dec)	β_c (mV/dec)	I.E. (%)	I_{pas} (mA/cm^2)
0	-690	100	> 400	195	---	630
200	-645	90	> 400	190	10	501
500	-730	63	> 400	175	37	398
1000	-655	57	> 400	165	43	316
1500	-720	54	> 400	155	46	251
2000	-640	52	> 400	140	48	158
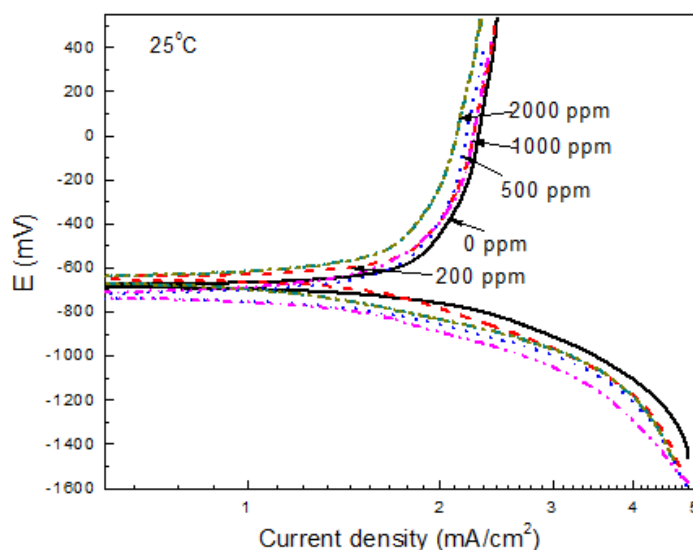
Figure 4. Effect of *Hibiscus sabdariffa* concentration on the polarization curves for pure Al in 0.5 M H$_2$SO$_4$ at 25^{0}C.

Polarization curves for pure Al in 0.5 M H$_2$SO$_4$ at different *Hibiscus sabdariffa* concentrations and 25^{0}C are shown in Fig. 4.
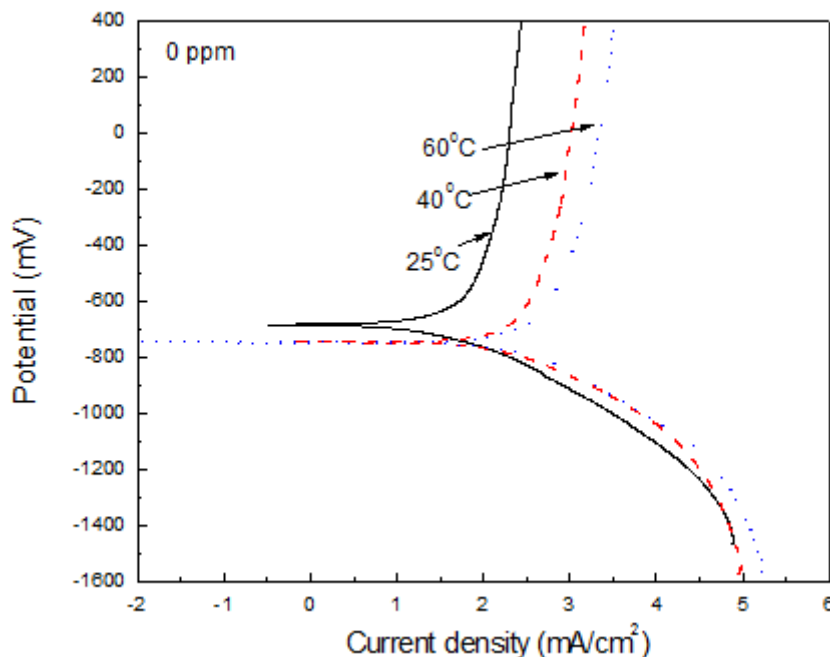
Figure 5. Effect of testing temperature in the polarization curves for pure Al in 0.5 M H$_2$SO$_4$ solution containing 0 ppm of *Hibiscus sabdariffa.*
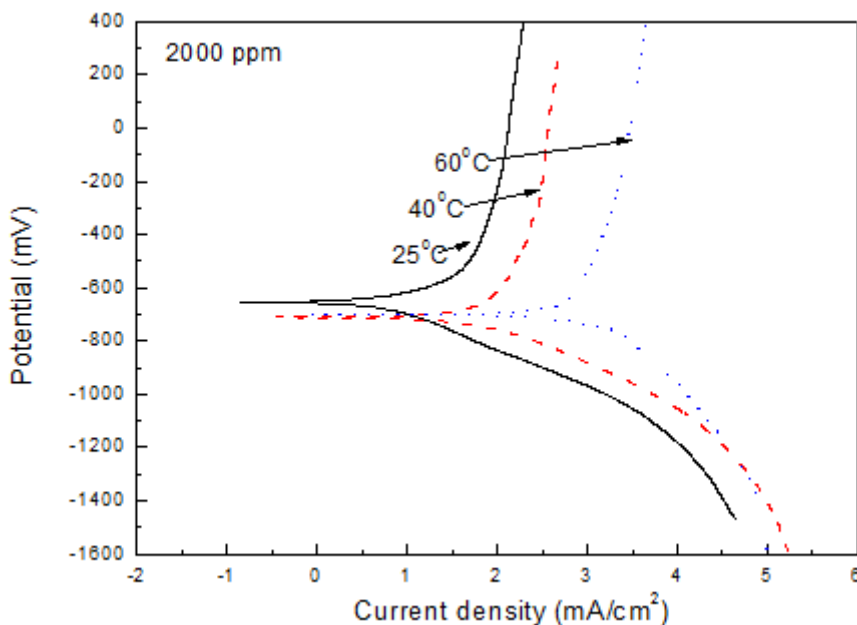

Figure 6. Effect of testing temperature in the polarization curves for pure Al in 0.5 M H$_2$SO$_4$ solution containing 2000 ppm of *Hibiscus sabdariffa.*

This figure shows that Al displays an active-passive behavior in this solution regardless of the presence of *Hibiscus sabdariffa*. This figure shows that in th blank, uninhibited solution, Al displays

an active-passive behavior with an E_{corr} value close to -690 mV and a corrosion current density value around 2.0 mA/cm^2. As the potential is made more anodic, the current density starts to increase untill it reaches a stable value which does not change with a further increase in the applied potential and the formation of a passive layer takes place. Both anodic and cathodic current density values decreased with the addition of *Hibiscus sabdariffa* and the establishment of the passive layer takes place also. Electrochemical parameters obtained from this figure are shown in table 1, where it can be seen also that anodic Tafel slopes are too high, and remained unchanged with the addition of *Hibiscus sabdariffa* extract. However, cathodic Tafel slope was decreased with the addition of the inhibitor, indicating the anodic character of *Hibiscus sabdariffa*. The passivation is due to the formation of corrosion products which makes more difficult the access of the electrolyte to corrode the underlying metal. Corrosion current density values also decreased with the addition of the inhibitor, reaching the lowest value when 2000 ppm of *Hibiscus sabdariffa* were added, but the E_{corr} value had a random variation with the addition of the inhibitor. It has been proved that Al is spontaneously passivated when exposed to oxygen in the atmosphere, and its exposition to 0.5 M H_2SO_4 reinforces this passivating layer since the passivation current density value, I_{pas} decreases with the addition of the inhibitor.

The effect of testing temperature in the polarization curves for both uninhibited and solution containing 2000 ppm of *Hibiscus sabdariffa* is shown in Figs. 5 and 6 respectively. It is clear that an increase in the temperature brings an increase in both the current density and corrosion current density values regardless of the presence of *Hibiscus sabdariffa*. In all cases, however, the alloy displayed an anodic limit current density value, a passive region, indicating the protective nature of the formed corrosion products. For the uninhibited solution, it is due to the formation of an aluminum oxide, Al_2O_3, but in presence of the inhibitor, it must be a complex corrosion product formed by this oxide and the inhibitor which in insoluble in the solution, but as the temperature increases, its solubility increases also, decreasing its protectiveness. 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:

$$Inh_{sol} + xH_2O_{ads} \rightarrow Inh_{ads} + xH_2O_{sol} \qquad [5]$$
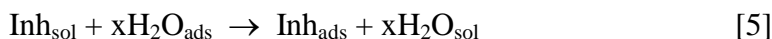
The inhibitor may then combine with freshly generated Al^{3+} ions on metal surface, forming metal-inhibitor complexes [30, 31]:

$$Al \rightarrow Al^{3+} + 3e \qquad [6]$$

$$Al^{3+} + Inh_{ads} \rightarrow [Al\text{-}Inh]_{ads}^{2+} \qquad [7]$$
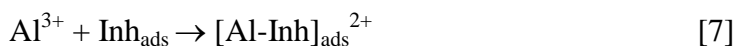
The resulting complex, depending on its relative solubility, which increases with the temperature, can either inhibit or catalyze further metal dissolution or increase its corrosion rate.
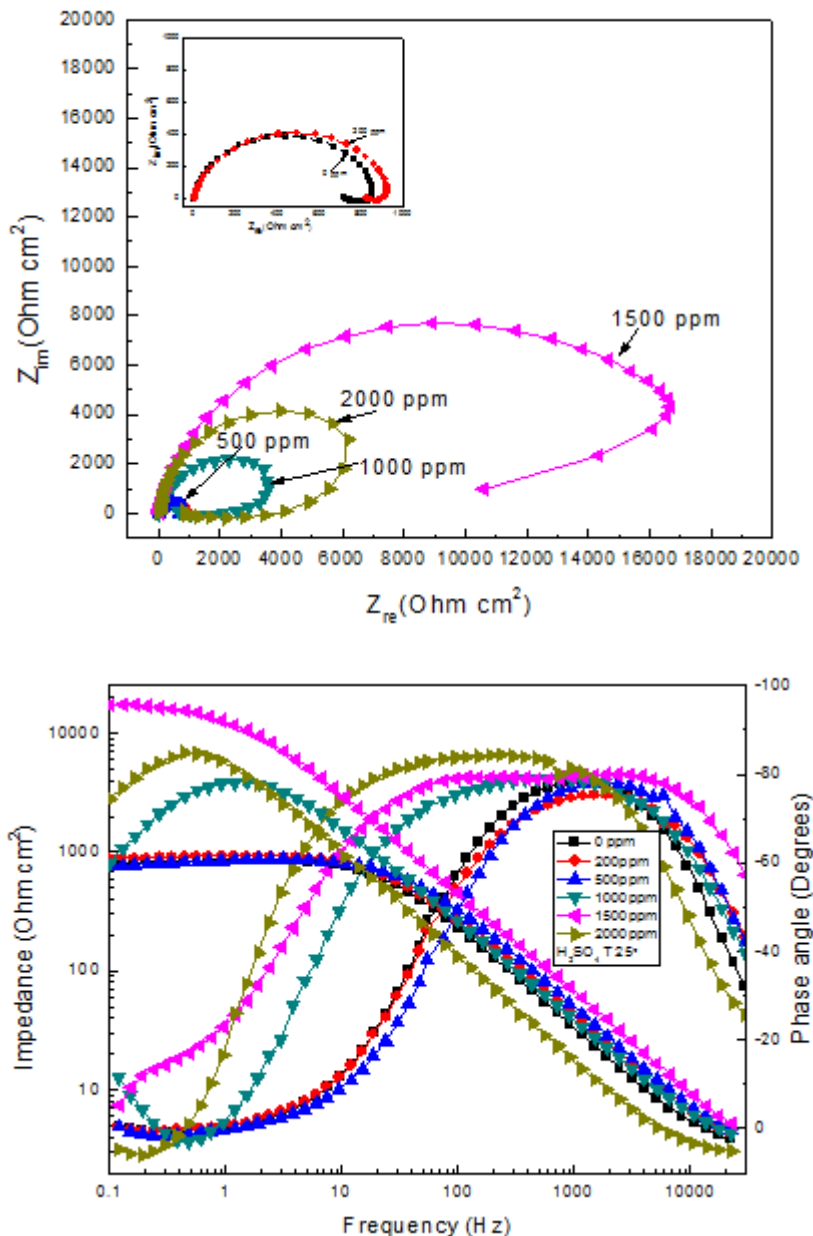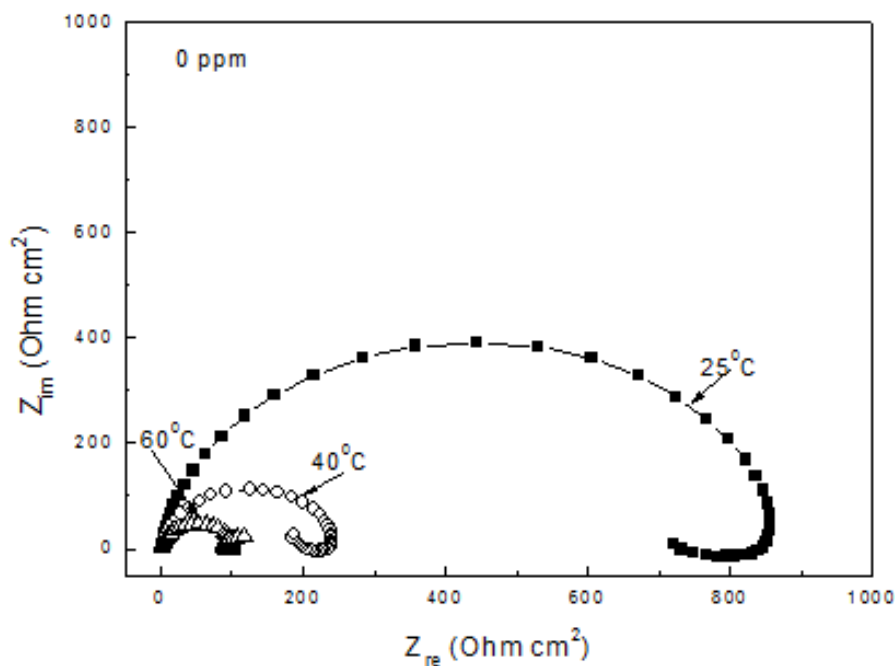
Figure 7. Effect of *Hibiscus sabdariffa* concentration on a) Nyquist and b) Bode plots for pure Al in 0.5 M H$_2$SO$_4$ at 25^{0}C.

The effect of *Hibiscus sabdariffa* concentration in the Nyquist and Bode plots for pure Al in 0.5 M. H$_2$SO$_4$ is shown in Fig. 7. Nyquist plot for the blank, uninhibited solution, Fig. 7 a, display a depressed, capacitive-like semicircle with its center in the real axis at high and intermediate frequency values, but at lower frequencies, data display an inductive loop. The high-frequency capacitive loop can be attributed to the charge transfer resistance (R$_{ct}$) whereas the inductive loop might have been caused by the adsorbed intermediate, probably Al(OH)$_3$ [22]. With the addition of *Hibiscus sabdariffa* the shape of the loop did not change, only increased in its diameter, and thus the R$_{ct}$ value, which indicates that the adsorption of the inhibitor decreases the corrosion rate and that the inhibition category under this condition belongs to geometric blocking [32, 33]. Bode plot, on the other hand,

Fig. 7 b, shows that the addition of *Hibiscus sabdariffa* led to an increase in the electrode impedance. However, the absence of linear log Z relations with a slope of -1 (especially in the case of an uninhibited system) and the departure of phase angle at intermediate frequencies from 90^0 shows that the circuit tends to the resistive behavior [34]. However, the region where the angle phase remained constant as the frequency decreased was wider in presence of *Hibiscus sabdariffa* than in the uninhibited solution, indicating a more protective passive formed film by the inhibitor.

Table 2. Effect of testing temperature in the inhibitor efficiency values obtained from polarization curves and EIS measurements.

	Polarization curves					EIS		
	0 ppm		2000 ppm			0 ppm	2000 ppm	
	E_{corr} (mV)	I_{corr} (mA/cm^2)	E_{corr} (mV)	I_{corr} (mA/cm^2)	IE (%)	R_{ct} (Ohm cm^2)	R_{ct} (Ohm cm^2)	IE (%)
25^0C	-690	100	-650	20	80	860	16675	94
40^0C	-745	200	-700	63	68	230	1500	84
60^0C	-745	500	-700	400	20	100	200	50

Figure 8. Effect of testing temperature in the polarization curves for pure Al in uninhibited 0.5 M H$_2$SO$_4$ solution.
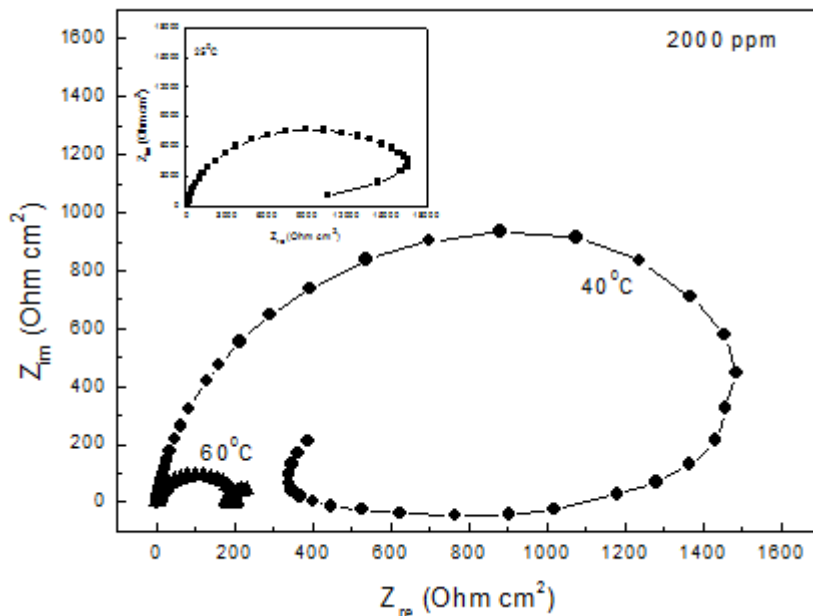
Figure 9. Effect of testing temperature in the Nyquist plots for pure Al in 0.5 M H_2SO_4 solution containing 2000 ppm of *Hibiscus sabdariffa*.

Table 3. Effect of *Hibiscus sabdariffa* concentration in the R_{ct}, C_{dl} and inhibitor efficiency values obtained from the EIS measurements at 25^0C.

C_{inh} (ppm)	R_{ct} (Ohm cm^2)	C_{dl} ($\mu F/cm^2$)	I.E. (%)
0	860	92.7	___
200	870	91	4
500	928	86	7
1000	3620	55	76
1500	6172	26	86
2000	16675	12	95

Nyquist diagrams for uninhibited and inhibited solution containing 2000 ppm of *Hibiscus sabdariffa* at different temperatures are shown in Figs. 8 and 9 respectively. It is clear that in all cases, an increase in the testing temperature brings a decrease in the semicircle diameter, indicating an increase in the corrosion rate as the temperature increases. However, it must be noticed that for the tests at 60^0C three loops could be observed: one capacitive loop at high frequencies, a second inductive loop at intermediate frequency values, and a third capacitive loop at low frequency values. The first capacitive loop is related with the charge transfer process through the double electrochemical layer, whereas the second, inductive loop, is related to the adsorption of an intermediate species, probably $Al(OH)_3$ [22]. Finally, the third capacitive loop is due to growth of the external protective film [22].

Table 2 gives a summary of the effect of the testing temperature in the inhibitor efficiency value as obtained vy using polarization curves and electrochemical impedance spectroscopy measurements. This table shows that, as in the weight loss measurements, the inhibitor efficiency value decreases with increasing the testing temperature, indicating the inhibitor degradation, an increase in the solubility of the complex formed by the inhibitor on the metal surface as the temperatures increases, thus, an increase in the corrosion rate.

Values of R_{ct}, C_{dl} and IE% for inhibited and uninhibited systems were estimated and are listed in table 3. Complete inspection of table 2 reveals that R_{ct} values increased with increasing inhibitor concentration. On the other hand, the values of C_{dl} decreased with an increase in *Hibiscus sabdariffa* concentration. This was a result of increasing surface coverage by the inhibitor, which led to an increase in IE%. The thickness of the protective layer, δ, was related to C_{dl} by the following equation [35]:

$$\delta = \varepsilon_0 \varepsilon_r / C_{dl} \qquad\qquad [8]$$

where ε is the vacuum dielectric constant, and ε_r is the relative dielectric constant. Thus, the decrease in the C_{dl} value, which can result from a decrease in the local dielectric constant and/or an increase in the thickness of electrode double layer, suggested that the inhibitor species perform by adsorption at the metal/solution interface [36,37] just as stated above in Fig. 3.

To establish whether inhibition is due to the formation of an organic film on the metal surface, scanning electron micrographs were taken. Fig. 10 shows the SEM micrograph of the Al surface before and after of the immersion in 0.5 M H_2SO_4 at 25 ^{0}C with and without corrosion inhibitor. This figure shows a chemical microanalysis done on the corroded metal surfaces also. It is evident from these SEM micrographs that the Al surface was strongly damaged in the absence of the *Hibiscus sabdariffa* with the increased number and depth of the pits and intergranular corrosion.
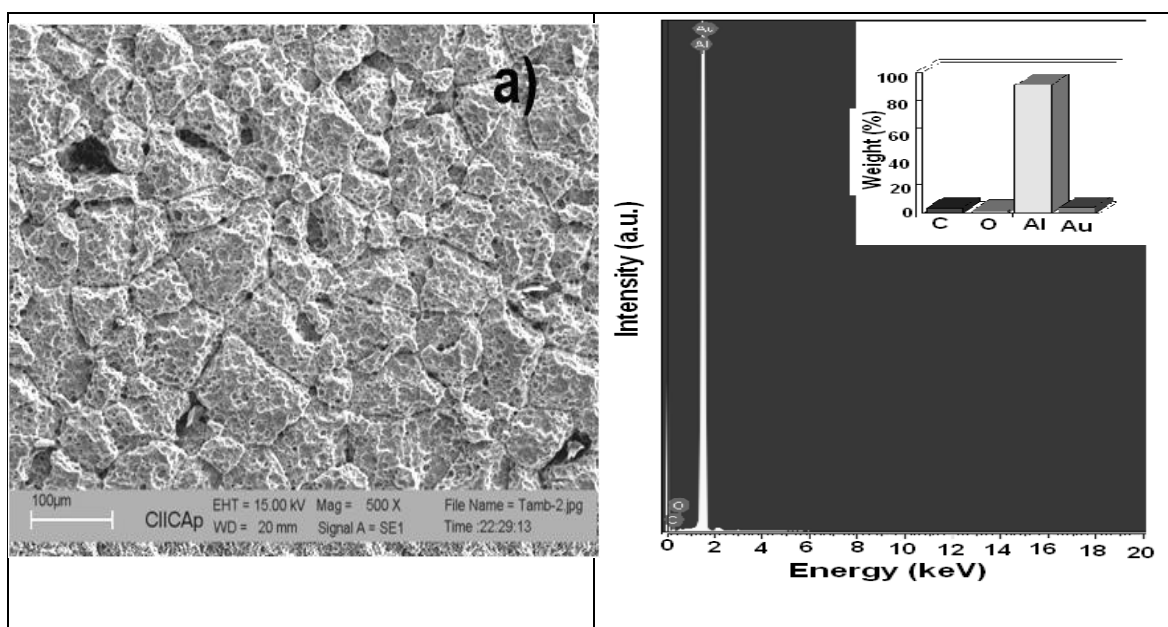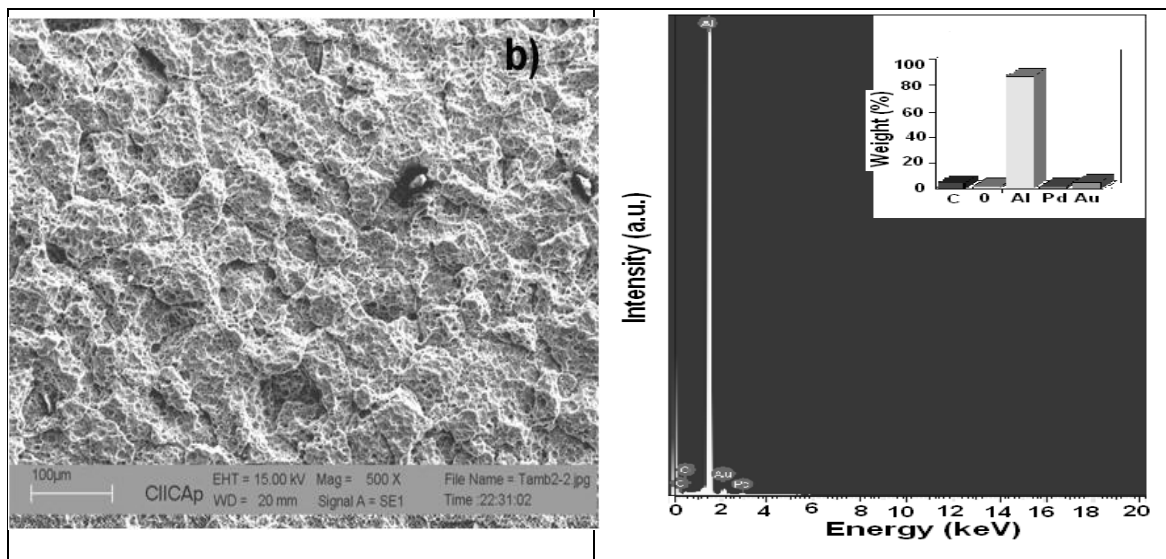
Figure 10. Micrographs of Al corroded in 0.5 M H_2SO_4 containing a) 0 and b) 2000 ppm of *Hibiscus sabdariffa* together with their chemical microanalysis at 25^0C

However, there are less pits and cracks observed in the micrographs in the presence of *Hibiscus sabdariffa* (Fig. 10 b) which suggests the formation of a protective film on the Al surface which was responsible for the decrease in the corrosion rate. In fact, *Hibiscus sabdariffa* can be regarded as good inhibitor for Al corrosion in sulfuric acid as evidenced by the results given above.

In order to have a better idea of which components of this plant extract are responsible for the decrease in the corrosion rate of Al, an FTIR analysis was performed, and the results are shown in Fig. 11, which shows the presence of

a width signal in 3408 cm^{-1} assigned for the O-H bond. The double C=C bonds of the aromatic ring were observed for the vibration in 1181 cm^{-1} and the C-H bonds of the aromatic ring were observed for the stretching band at 2361 cm^{-1}. In 1741 cm^{-1} was observed the signal for the C=O bond, assigned to a carbonyl group. The ether group was observed at 1069 cm^{-1}. The IR spectrum analysis confirmed the *Hibiscus sabdariffa* extract contained flavonoid compounds which have a chemical structure as shown in Fig. 12. The presence of functional groups such as OH may be one of the responsible for the decrease in the corrosion rate, since they can react with the Al^{3+} ions released during the oxidation of Al according to

$$Al^{3+} + 3(OH^-) \rightarrow Al(OH)_3 \qquad\qquad [9]$$

Because of the insolubility of $Al(OH)_3$ in the solution they accumulate at the metal/solution interface of the electrode resulting in the formation of protective corrosion products layer. The adsorption of $Al(OH)_3$ has been reported to be the responsible for the inductive loop observed in the Nyquist diagrams shown in Figs. 7-9 as explained above [22]. The high inhibitive performance of this plant extract suggests a strong bonding of the *Hibiscus sabdariffa* derivatives on the metal surface due to presence of lone pairs from heteroatoms (oxygen, carbon) and π-orbitals, blocking the active sites and therefore decreasing the corrosion rate. Accordingly to [27], it was expected that water-soluble

organic constituents (thiamine, niacin, ascorbic acid, and anthocyanins) of *Hibiscus sabdariffa* petals may play an important role in the inhibition mechanism of Al corrosion in the tested solutions. Accordingly, the positively charged species in *Hibiscus sabdariffa* (thiamine and anthocyanins) was expected to adsorb under electrostatic attraction with the negatively charged Al surface giving rise to physical adsorption mechanism.
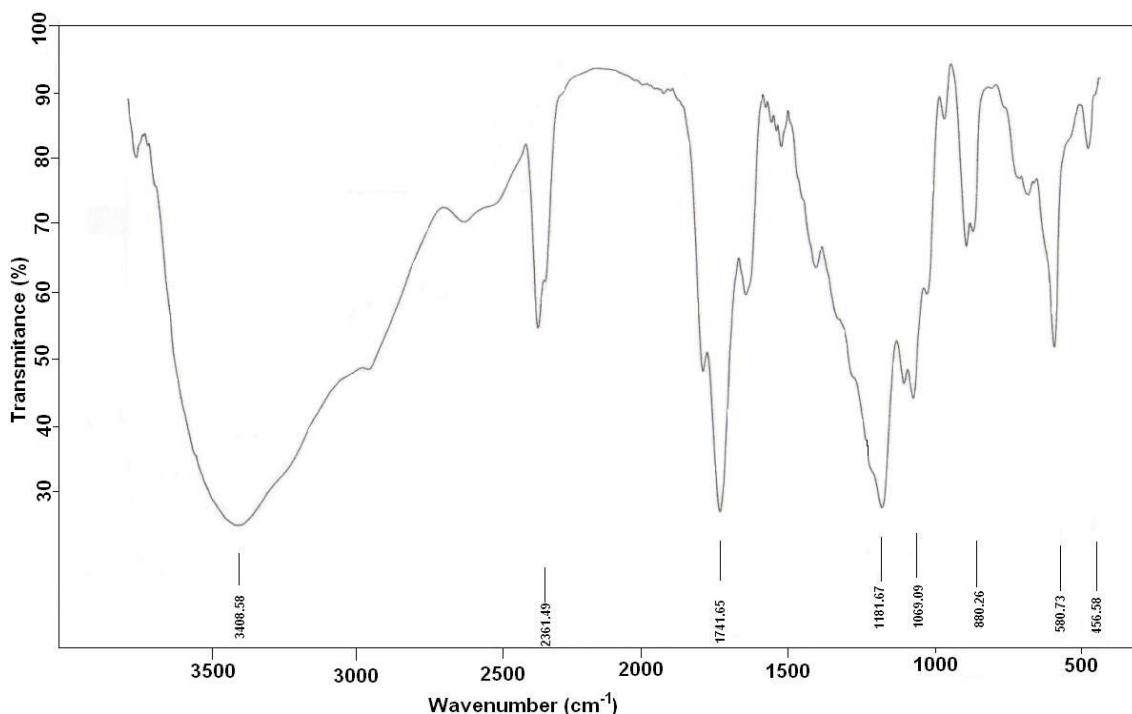
Figure 11. IR spectrum of *Hibiscus sabdariffa* extract
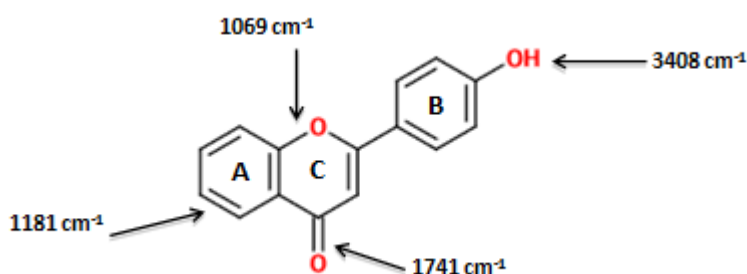
Figure 12. The important functional groups in general structure of flavonoids and their IR frequencies

4. CONCLUSIONS

The use of *Hibiscus sabdariffa* as inhibitor for the corrosion of pure Al in 0.5 M H_2SO_4 at 25, 40 and 60^{0}C has been evaluated by using gravimetric tests, potentiodynamic polarization curves and EIS measurements. It was found that

Hibiscus sabdariffa extract is a good inhibitor for pure Al, whose efficiency increased with its concentration but decreasing with the testing temperature. *Hibiscus sabdariffa* decreased both the anodic and cathodic current density values, behaving thus as a mixed type of inhibitor, which was physically absorbed on the metal surface following a Langmuir model. The reduction in the corrosion rate was due to the presence of flavonoids in the plant extract which contains from heteroatoms (oxygen and carbon) and □-orbitals, blocking the active sites on the metal.

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