

Sargassum Extract As A Biological Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid

G. Serrano-Villanueva¹, L. P. Alvarez-Berber², E. C. Menchaca-Campo¹, and J. Uruchurtu- Chavarín¹

1. Universidad Autonoma del Estado de Morelos- CIICAp, Mexico

2. Universidad Autonoma del Estado de Morelos- CIQ, Mexico

Abstract: The metallic corrosion inhibition effect of the invasive brown seaweed Sargassum (natans and fluitans) extract, harvested from the Caribbean sea in the coast of Mexico, against the corrosion of carbon steel in 0.5 M HCl medium was studied using electrochemical techniques namely: polarization resistance, impedance, and noise measurements. The hexane and di-chloride methane crude extracts of Sargassum is rich in alginate biopolymer. The corrosion evaluation tests showed that this algal extract acts as corrosion inhibitor for carbon steel substrate in 0.5 M HCl since inhibition efficiency of 93% was reached with 1 g/l of Sargassum extract at room temperature. AC impedance findings showed that the seaweed extract adding in the corrosive electrolyte increases the polarization resistance and conversely decreases the double layer capacitance at the interface. Adsorption of Sargassum on the substrate surface followed the Langmuir adsorption isotherm demonstrating that the corrosion inhibition mechanism of carbon steel substrate in 0.5 M HCl environment by the investigated algal extract is typical of the physisorption process and the protective barrier is mainly formed by the adsorbed biological macromolecules.

Key words: sargassum, corrosion protection, inhibitor, biopolymer

1. Introduction

In the middle of the past century a common argument was economic growth against environmental protection that was pollution against clean environment. With the expansion of the global economy, industrial development and fossil fuel production and utilization increased, came climate change with its full consequences, not yet completely foreseen. This development creates wastes polluting the environment, with the production of toxic chemicals and many other products. Nowadays with increasing concern for the environment and its conservation and scarce economic resources, efficiency is paramount pushing the need for: alternative energy sources, recycling, development and consumption of environment friendlier resources and chemicals to substitute toxic chemicals.

Metals are widely used as construction materials in industry, but in its pure form are thermodynamic unstable and may suffer degradation from corrosion. Corrosion process is a complex phenomenon involving corrosion products or oxide film formation. These products are formed by a few brittle oxide and hydroxide surface layers, in many cases of different colors and textures by the reaction with environmental reactant contents. These cause economic loss, safety concern and even loss of life [1].

Nowadays, research is focused on the development, synthesis, manufacture and use of materials and chemicals environmentally friendly, aiming to substitute the traditional polluting materials and toxic chemicals. Furthermore, various biopolymers are being tested and used as green metallic corrosion inhibitors friendly with the environment [2, 3].

Steel materials are very important in a wide variety of industrial applications due to their excellent mechanical properties and low cost. Nevertheless,

Corresponding author: Jorge Uruchurtu Chavarin, Ph.D., research area: Materials Science. E-mail: juch25@uaem.mx.

these metals are somewhat unstable in certain aggressive media, mainly acid cleaning process in the oil and gas industries and cleaning of boilers in the production of thermal energy and industrial processes. In all of these, the use of corrosion inhibitors is one of the most economic, successful, and effective means to protect against metallic corrosion in acid media. Recently the search had taken to the evaluation of plants and algae as green inhibitors [4].

Biopolymers are presented as a class of efficient corrosion inhibitors, showing a good compatible ability with metal ions, covering a wide surface area of the metal. It was reported sargassum muticum extract as an efficient mixed biological inhibitor against corrosion of carbon steel in acid medium, exhibiting phenolic compounds. The inhibitor efficiency increased as a function of concentration [4-6].

The aim of the present work was to evaluate the use of brown algae sargassum as a possible steel corrosion inhibitor in chloride acid. To perform this task the extract was obtained and added to the corrosive solution at different concentrations to obtain its efficacy and efficiency applying electrochemical techniques.

2. Experiment Procedure

Sargassum from the beaches of Cancún, Quintana Roo, Mexico was collected. The excess sand was necessary to remove by means of washing in abundant tap water and afterwards it was left to dry indoors at ambient temperature for four days. Once dried it was grounded to obtain sargassum dry powder to prepare hexane or dichloromethane extract. To obtain these extracts a Soxhlet equipment was used connected to a recirculatory system to maintain the refrigerating temperature. Solvent recovery was developed in similar way using the Soxhlet equipment. Once the extract was dried and weighed in an analytical balance, afterwards, the dissolutions for electrochemical evaluation were made at different concentrations.

3. Sample Preparation

Carbon steel cylinders were cut to obtain an exposed area of 0.71 cm^2 , then sample probes were immersed in glacial acetic acid solution for two hours (20:80), then removed and washed in distilled water and brushed off corrosion products from the metal surface with a soft brush. Copper wires 15cm long were soldered in the back of the steel samples, and then they were encapsulated using an epoxy resin and left to dry at room temperature. Afterwards the surface was abraded with 600-1200 carbide paper reaching a mirror like surface cleaned with ethanol and left to dry, ready for testing.

4. Electrochemical Evaluation

Metallic probes were evaluated in 0.5 M HCl solution with different extract concentrations using electrochemical techniques and compared with the blank sample. An electrochemical cell was used consisting of two steel working electrodes, a saturated calomel reference electrode and a graphite rod as an auxiliary electrode. The cell was connected to a Gill AC (ACM Instruments) potentiostat [8].

Triplicate measurements were made sequentially, to avoid alterations in the electrochemical interface from electrochemical polarization. First electrochemical noise measurements were performed in two nominally "identical" and the reference electrodes. Electrochemical measurement rate was one measurement per second and 1024 data points were obtained and stored for further analysis. After trend removal using a least squared fitting the noise resistance (R_n) as a function of time, was obtained dividing each potential over a current data in analogy with Ohm's law.

After noise measurements then linear polarization resistance were performed on a working electrode, with the reference electrode and the auxiliary electrode through a $\pm 50 \text{ mV}$ (linear region) polarization curve around the corrosion potential (E_{corr}), obtaining the

linear relation $\Delta V/\Delta I$ and the polarization resistance (R_p).

Finally, the electrochemical impedance spectroscopy was performed in the three electrodes arrangement mentioned before, with a sweep in the frequency range of 10 kHz down to 0.05 Hz, with a 20 mV sinusoidal signal at the corrosion potential, obtaining the Nyquist diagram of real (Z_r) vs imaginary impedance (Z_{im}).

4.1 Scanning Electron Microscopy (SEM)

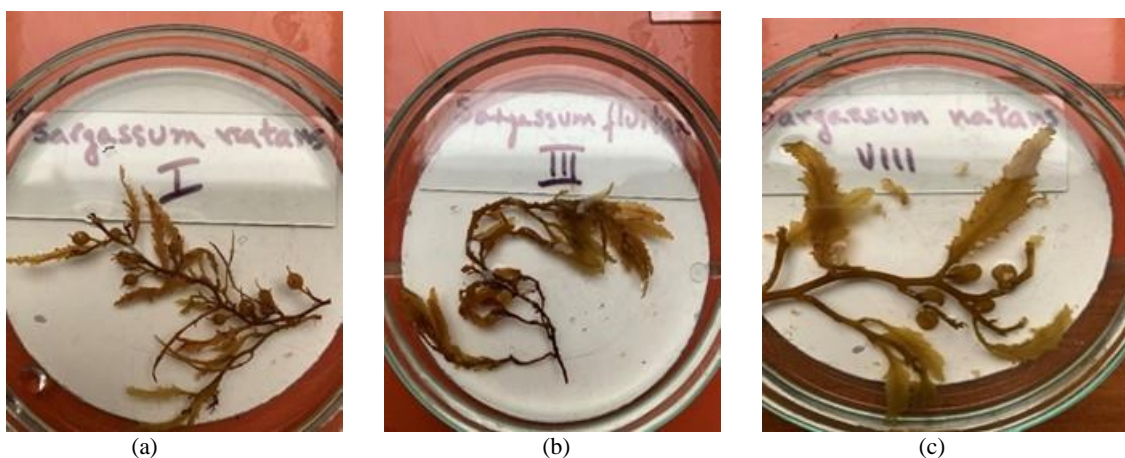


Fig. 1 Sargassum a) natans I, b) fluitans III, and c) natans VIII.

Sargassum inhibition evaluation were performed over two different polarity extracts: hexane (C_6H_{14}) and dichloromethane (CH_2Cl_2) at different concentrations (25, 50, 100 ppm) to obtain the better concentration as steel corrosion inhibitor in chloride acid 0.5 M solution [4, 9, 10].

As an example, in Fig. 2, the electrochemical potential and current noise-time series obtained for the

Three samples were used for SEM analysis after 24 hours of immersion in the acid solution: one the blank sample, another the 100 ppm hexane extract solution exposed sample and the third one the 100 ppm dichloromethane extract solution immersed sample. These analysis were made in a Jeol ISM-Series7600 SEM.

5. Results

For sargassum identification three morpho-species were found, generally reported as seen in Fig. 1 [4].

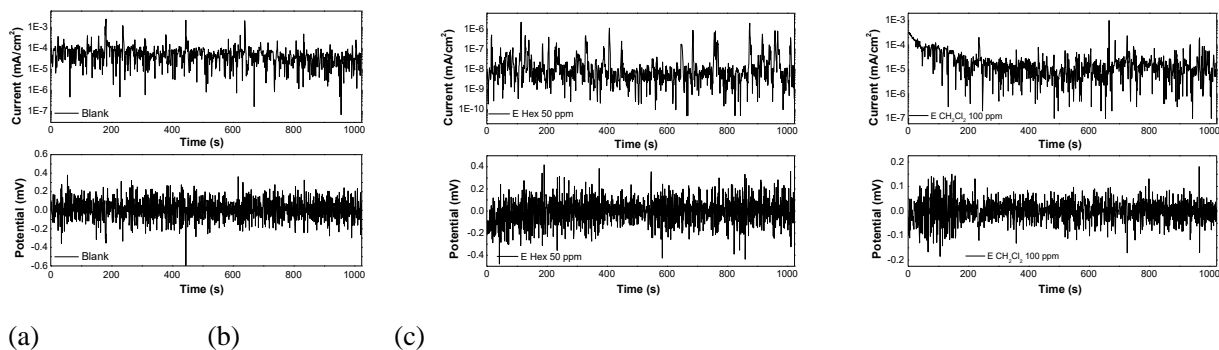


Fig. 2 Electrochemical potential and current noise time series for a) carbon steel, b) hexane extract 50 ppm and c) dichloromethane extract 100 ppm.

best concentration are presented: 50 ppm for hexane and 100 ppm for dichloromethane compared to the steel blank. From the electrochemical noise time series, it can be observed a random oscillating behavior typically related to uniform corrosion accompanied with variable sudden increase of higher amplitude transients or train of pulses, associated to localized corrosion events along the measurement period.

Table 1 presents the noise resistance (R_n) values obtained, where an increase with respect to the steel blank sample for both inhibitor extracts, can be observed. For the hexane extract, the greater noise resistance value corresponds to 100 ppm concentration, while for dichloromethane extract corresponds to 50 ppm [8].

Fig. 3 presents the polarization resistance curves to obtain the linear polarization resistance (R_p) for both extracts: hexane and dichloromethane, shown in Table 2. Also, the corrosion potential (E_{corr}) as a function of extract concentration is presented, and a slight increase

to noble values with respect to the steel blank sample corrosion potential, can be observed.

Table 1 Noise resistance values for uninhibited steel and different extracts concentrations.

Inhibitor Concentration	Steel R_n (ohms-cm ²)	Hexane R_n (ohms-cm ²)	Dichloromethane R_n (ohms-cm ²)
0	702	-	-
25	-	737	1370
50	-	881	4975
100	-	1900	1029

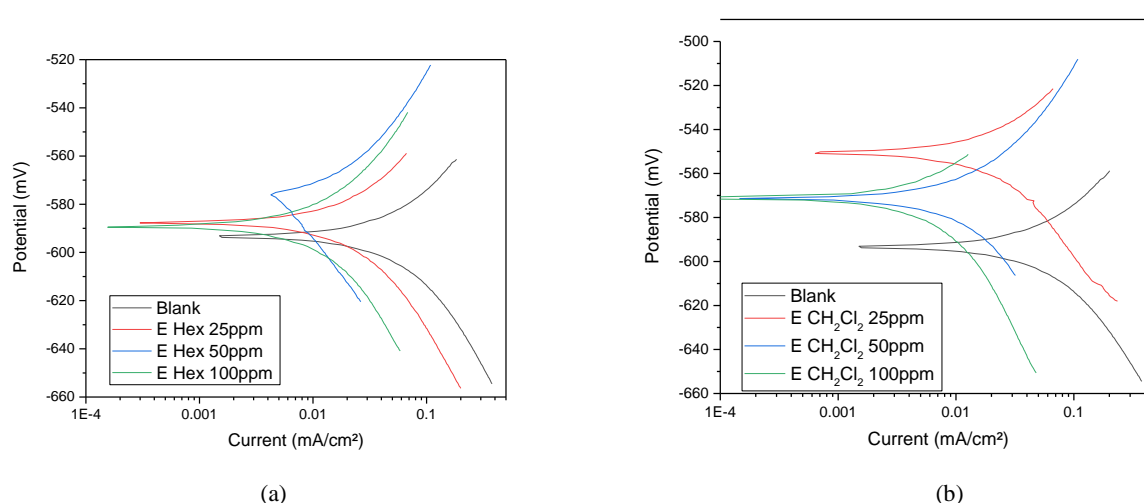


Fig. 3 Linear polarization curves for steel without and with: a) hexane extract and b) dichloromethane extract.

It can be observed the corrosion potential of -590mV_{SCE} for the steel blank sample in the acid medium without inhibitor, rose to nobler values reaching -575mV_{SCE} for hexane 50 ppm and -550mV_{SCE} for the 25 ppm dichloromethane extract solution. This suggests anodic inhibitor behavior over samples immersed in both extracts, becoming less prone to corrosive attack. These changes may be due to the sargassum extract molecules adsorption over the metallic surface improving its corrosion resistance in the chloride acid solution [11]. It can be mentioned there was no direct relation of the changes in corrosion potential with respect to extract concentration.

As far as the linear polarization resistance values obtained, they increased as a function of extract

concentration. For the 100 ppm concentration hexane extract the polarization resistance went up from 86ohms-cm^2 obtained for the uninhibited steel to 866ohms-cm^2 . For the dichloromethane extract the increase reached 1330ohms cm^2 (Table 2), hence diminishing the corrosion rate.

Inhibition efficiency was calculated according to the following equation using values obtained from the linear polarization resistance, presented in Table 2:

$$E (\%) = [(R_{p_{inh}} - R_{p_{blank}}) / R_{p_{inh}}] \times 100$$

The best efficiencies obtained were 90% for 100 ppm hexane extract concentration and 93% for dichloromethane at the same concentration. Nevertheless, it had to be mentioned that for the latter extract, at half the concentration (50 ppm), the

efficiency was 90% [12, 13], just 3% below. These efficiencies compared favorably with reports made in the literature [4].

From the electrochemical impedance spectroscopy technique and analysis, the Nyquist diagrams were obtained for the evaluation of steel corrosion in 0.5 M HCl solution and inhibition of the extracts tested and presented in Fig. 4. The steel sample diagram presents a depressed capacitive semicircle associated to the charge transfer reaction. This is typical for steel corrosion in acid media where uniform corrosion is present over the whole surface.

For the different extracts concentrations two depressed capacitive semicircles were obtained and presented in Fig. 4. The first one associated to the charge transfer reaction, and the second to mass transport and adsorption process, possibly forming a protective film over the metallic substrate [14-17]. The second low frequency semicircle is associated to molecules adsorbed along with some corrosion products present. The frequency dispersion forming depressed semicircles are associated to the surface heterogeneities and other forms of interfacial phenomena [18-20].

Table 2 Corrosion potential, polarization resistance and inhibition efficiency for hexane and dichloromethane extracts in HCl 0.5 M.

Concentration ppm	Hexane			Dichloromethane		
	E _{corr} mV	R _p (ohms cm ²)	Efficiency %	E _{corr} mV	R _p (ohms-cm ²)	Efficiency %
0	-593	86	-	-593	86	-
25	-587	433	80	-550	130	33
50	-575	520	83	-571	866	90
100	-589	866	90	-571	1330	93

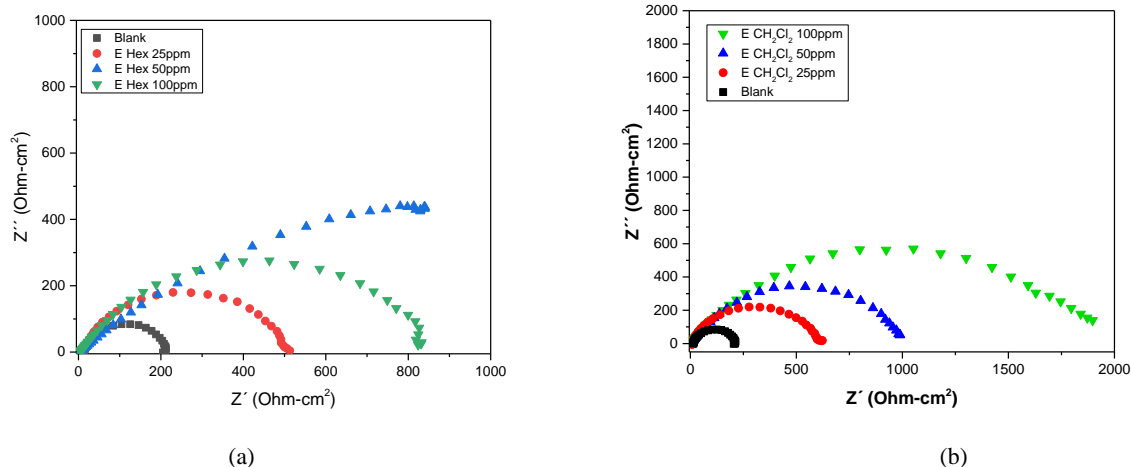


Fig. 4 Electrochemical impedance Nyquist diagram for the extracts evaluation as inhibitors for different concentrations: a) hexane and b) dichloromethane.

The electrochemical impedance values were fitted using the Zview software. The fitting circuit used and presented in Fig. 5, including a solution resistance (R_s) in series with two RC parallel loops with capacitance values fitted with constant phase elements due to semicircles depression representing the absence far from ideal capacitors. This is a common practice in

electrochemical circuit parameters fitting [8, 20-22]. In the case of steel (blank) sample the circuit reduces to a typical RC Randles equivalent circuit.

Table 3 presents the equivalent circuit electrochemical fitted parameters for the steel sample without and with possible inhibitor's evaluated extracts, for the best concentration in both cases (100 ppm).

Although, for dichloromethane extract the charge transfer resistance (R_{ct}) increased almost 10 times its value with respect to the steel blank sample.

The addition of the inhibitor extracts modifies the Nyquist diagrams with the appearance of second sometimes incomplete depressed semicircle and a second time constant as a product of the inhibitor resistance and capacitance ($R_{inh} C_{inh}$) associated to the adsorption of extract molecules added up, modifying the corrosion mechanism, changing the effect with the extract concentration, arc distortion or depression may result [20-22].

Table 3 Equivalent circuit for electrochemical impedance data fitting for hexane and dichloromethane best concentration (100 ppm).

Sample	R_s cm ²	R_{ct} cm ²	n_1	C_{dl} F/cm ²	R_{inh} cm ²	n_2	C_{inh} F/cm ²
Blank	3.7	83	0.734	8.02E-5	-	-	-
Hexane	9.9	488	0.669	3.2E-7	462	0.69	3.16E-6
Dichloromethane	8.1	800	0.726	3.3E-7	884	0.431	4.8E-6

This is reflected in the n (depression angle) values lower than 0.8, from the equivalent circuit data fitting of electrochemical parameters, where constant phase elements were used instead of ideal capacitors as reported [21, 22]. The magnitude of the charge transfer and inhibitor resistance, as well as the total impedance modulus reflect the decrease in corrosion rates as a function of extract concentration and consequently better protection, as presented in Table 3. The inhibitor protective film adsorbed over the metal surface acts as an active barrier to the aggressive attack from the corrosive acid medium.

Hexane and dichloromethane extracts are adsorbed in the metallic surface, therefore different types of adsorption isotherms such as: Langmuir, Temkin or Frumkin are required to be used. According to Fig. 6, the best adsorption isotherm fitting is the Langmuir isotherm, occurring between the metal surface and the extract given by the following expression:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

$$\theta = \frac{\text{inhibidor efficiency}}{100}$$

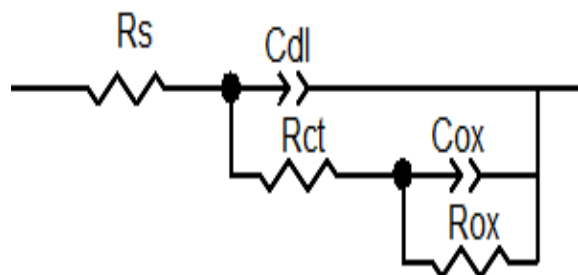


Fig. 5 Equivalent circuit for electrochemical impedance data fitting.

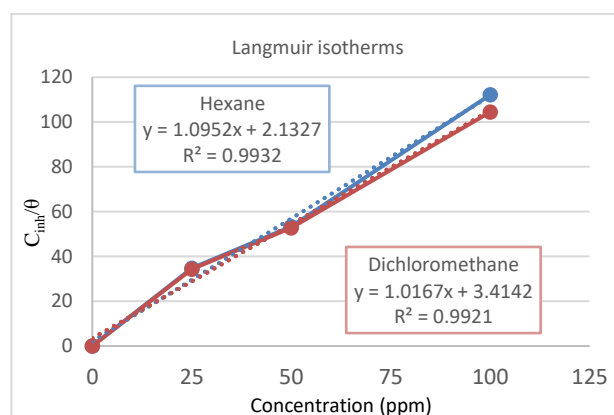


Fig. 6 Langmuir isotherms for hexane and dichloromethane extracts.

The correlation was obtained from the plot of concentration over the fractional surface coverage (θ), against the extract concentration (C_{inh}) as shown in Fig. 6.

From the graph the slope of the straight line can be obtained equal to $\frac{1}{K_{ads}}$, being K_{ads} the adsorption constant. The Gibbs adsorption free energy (ΔG°_{ads}) can be determined using the following expression:

$$\Delta G^{\circ}_{ads} = -RT \ln (55.5 K_{ads})$$

where R is the ideal gases constant (8.3144 J/mol K), T the temperature in Kelvin degrees (298.15K) and 55.5 corresponds to the water molar concentration in solution. The Langmuir isotherms present 99% correlation for both extracts, with 1.09 and 1.01 slopes of hexane and dichloromethane respectively. The Langmuir isotherm assumes no interaction exists between adsorbed molecules on the steel surface [23-25].

If $\Delta G^\circ_{\text{ads}}$ present negative values meaning inhibitor molecules adsorbs spontaneously over the metallic surface. When $\Delta G^\circ_{\text{ads}} < -20 \text{ kJ mol}^{-1}$ or less negative is assumed as physisorption, and chemisorption when

$\Delta G^\circ_{\text{ads}} > -40 \text{ kJ mol}^{-1}$ or more negative [26-29]. Between these ranges it is considered a mixed mechanism, as in this case it is considered a physisorption mechanism.

In SEM micrographs, shown in Fig. 7 (a-c), metallic surfaces comparison can be observed at the same scale (500X): blank, hexane and dichloromethane at 50 ppm and 100 ppm extract concentrations, respectively.

Table 4 Gibbs adsorption free energy.

Extracts	K_{ads}	$\Delta G^\circ_{\text{ads}}$ (kJ/mol)
Hexane	0.7819	-9.34
Dichloromethane	0.9210	-9.75

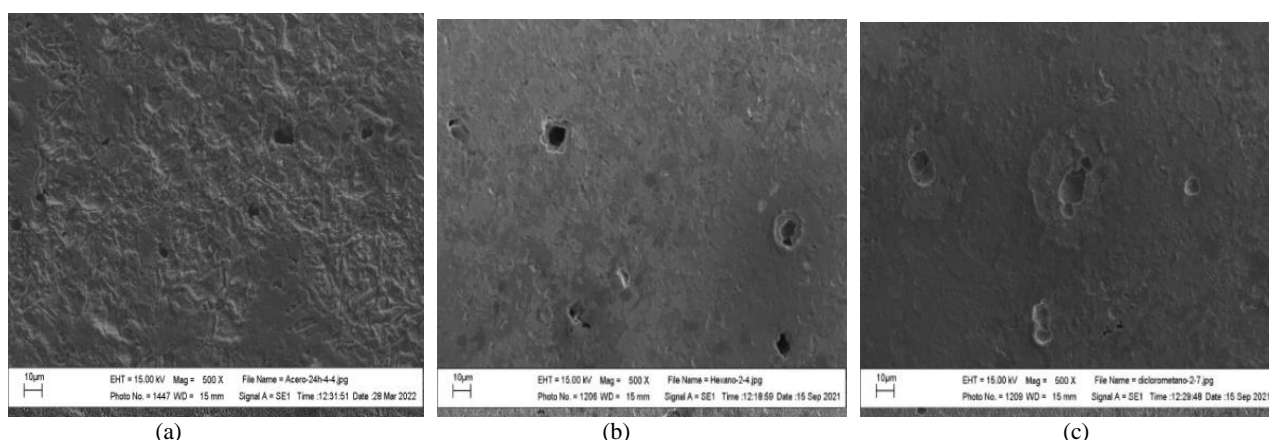


Fig. 8 SEM micrographs for steel samples (500X) immersed for 24 hours in the HCl 0.5M solution: a) blank, b) Hexane 50 ppm and c) Dichloromethane 100 ppm.

The blank sample presents typical uniform corrosion attack and surface wear for steel in acid electrolytic media. Hexane micrograph shows less superficial wear and localized pitting attack ascribed to protective film formation from corrosion products or hexane extract and localized rupture. Similar features were observed for dichloromethane after 24 hours of immersion. Deeper pits suggest a better film formation and protection, therefore even more localized attack. Some coalescent pits growing side by side, can be observed [30, 31].

6. Conclusions

The sargassum brown algae from the coast of the Mexican caribbean sea, presents good properties as steel

corrosion inhibitors in HCl 0.5 M acid solution. Corrosion rate diminished almost ten times, and efficiency as a function of concentration reached 93% for dichloromethane 100ppm concentration, according to linear polarization resistance. Electrochemical impedance demonstrates the increase in charge transfer resistance and changes observed in the capacitance values, due to the addition and adsorption of algae extract molecules over the steel surface, in agreement with the Langmuir isotherm model of physisorption proposed. Electrochemical noise measurements suggest localized pitting surface attack over the inhibited metal, corroborated by SEM characterization. It remains to be studied the good corrosion protection

from sargassum extracts as a function of time of immersion and the residence time.

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