Green Approach to Corrosion Inhibition of Carbon Steel by *Fucus spiralis* extract in 1 M HCl Medium

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Abstract: The extract of Fucus spiralis (FS) was tested as a corrosion inhibitor of carbon steel in a 1M HCl medium. The anti-corrosion properties were analyzed by gravimetric and electrochemical techniques such as potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). The surface characterization of carbon steel submerged in the optimal solution was carried out using UV-Visible, UV-Vis-NIR, and Optical microscopy analyses. Electrochemical and gravimetric results demonstrated that inhibitory efficiencies increase with increasing inhibitor concentration and the efficiency reaches 87% at a concentration of 0.5 g/L. According to Tafel extrapolated polarisation measurements, the FS also worked as a mixed-type corrosion inhibitor and changed the mechanism of anodic reactions. EIS analysis showed that a depressed capacitive loop dominates the Nyquist plot of impedance and enhances the polarization resistance (Rp) to 161.9 Ω cm² with a reduction of the double layer capacity (Cdl) of carbon steel to $61.8 \,\mu\text{F/cm}^2$. This protection is assured by an adsorption mechanism based on the isothermal Langmuir adsorption model, which positively affects the thermodynamic parameters. UV-Visible, UV-Vis-NIR analyses exhibited that inhibitor decreases the iron oxides like hematite, Magnetite, and Goethite, Maghemite, Lepidocrocite, δ -FeOOH of the metal surface and delays the dissolution of the bare metal of iron to the ferrous ions, notably that optical morphology showed that FS extract decreases the aggressivity of HCl.

Keywords: green inhibitor; carbon steel corrosion; electrochemical techniques; UV-Visible/UV-Vis-NIR; optical microscopy.

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1. Introduction

Carbon steel is frequently used in building materials, and in the industrial process, contact with the acidic environment can damage the material [1]. The study of steel corrosion has received considerable academic and industrial attention in an acidic environment [2–4]. Acid solutions are extensively employed in manufacturing processes like cleaning, descaling, pickling, and acidifying oil wells [5]. Over the past decade, to protect the steel from degradation and prolong its life, corrosion inhibitors have been considered the practical corrosion protection methods, notably in acidic solutions to prevent metal dissolution [6,7]. Thus, several organic chemical compounds were inspected. The researchers suggested that the electronegative property of the O, N, S, and P atoms and the properties of aromatic and unsaturated bonds are

responsible for inhibition effectiveness. Usually, this inhibitory performance is due to the adsorbent layer that forms on the metal due to the reaction between molecules of organic compounds and the unoccupied orbital of surface metal atoms [8–10]. Currently, due to a factor of toxicity to users and the environment, certain synthetic corrosion inhibitors are abandoned [11]. For that, researchers are interested in using essential oils and medicinal plant extracts as corrosion inhibitors [12,13]. Abdallah *et al.* [14] were related the inhibiting impact of some plants such as curcumin, parsley, and cassia bark extracts to the molecular size of the major component. The author has also studied the Nutmeg oil as a safe and green inhibitor for the corrosion of carbon steel type L-52 (CS L-52) in 1.0 M HCl, which was explained that the adsorption of nutmeg oil onto the surface of the CS follows the Langmuir isotherm [15].

In addition, the extract of *Fucus spiralis* (FS) has not been studied before, for that, the curiosity to know the behavior of the carbon steel in the presence of this extract leads us to publish this research document to explain the protection against corrosion of carbon steel in hydrochloric acid (HCl 1M), via a methanolic extract of *Fucus spiralis* (FS) through different procedures: mass loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), UV-Vis -NIR spectroscopy and optical microscopy technique.

2. Materials and Methods

2.1. Extraction of inhibitor.

Fucus spiralis (FS) is a type of alga that has a brown color, the origin of this species is the coastal area of Cape Ghir, 43 km northwest of Agadir (Morocco), which was collected at low tide. This alga is carefully rinsed and dehydrated to eliminate all traces of salt. Then, it is degraded to fine particles using an electric grinder. After that, 20g of powder was extracted for 3 hours by the methanol utilizing Soxhlet. The collected extract was concentrated by rotary evaporation, and the efficiency of the final product was about 13.25%.

2.2. Materials.

Carbon steel was used in this study with a chemical composition of 0.370% C, 0.230% Si, 0.680% Mn, 0.016% S, 0.077% Cr, 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160 % Cu and the rest is iron balanced. The samples are prepared before immersion in the solutions by an abrasive polishing paper with fine particles (220 to 1200), then cleaned by distilled water, followed by a stream of hot air.

2.3. Preparation of the solutions.

Simulation of the aggressive environment was obtained using a hydrochloric acid solution (1M HCl) from analytical grade (37% HCl). The corrosive medium of 1 M hydrochloric acid was chosen because hydrochloric acid is a commonly used mineral for acid cleaning and descaling. The inhibitor used in our study is the methanolic extract of FS. The range of inhibitor concentrations varied from 5×10^{-2} g/L to 0.5 g/L.

2.4. Gravimetric measurements.

In these measurements, we prepared the samples in closed glass vials containing 50 mL of the electrolyte by changing the concentrations of FS extract, the temperature of the test

solution was 303 K, and the immersion time was 6 hours. The experiments were achieved three times, and the average value of the mass loss was noted.

2.5. Electrochemical measurements.

The results of the electrochemical methods were measured employing three electrodes, saturated calomel electrode (SCE), platinum electrode, and carbon steel electrode (1 cm^2). The corrosion cell is linked to the VoltaLabpotentiostat (PGZ 100), controlled by the VoltaMaster 4 software. To achieve the stable state of the electrode/solution system, the working electrode is submerged for 30 min in the solution at open circuit potential (E_{ocp}). Then, the electrochemical impedance spectroscopy (EIS) results were executed by decreasing the frequency from 100 kHz to 10 mHz, with 10 points per decade, and the experiments were repeated three times. After the AC impedance test, the potentiodynamic polarization curve was drawn at the scan rate of 0.5 mV/s, from -800 mV/SCE to -200 mV/SCE.

2.6. Surface morphology and chemical composition.

The surface morphology of the samples was obtained by optical microscopy (Leica DM6000 M), and the surface reflectance spectra of the samples were achieved by UV-Vis diffuse reflectance spectroscopy at room temperature using UV-Vis-NIR spectrophotometer (Jasco V670 model), linked to the integrating sphere (ILN-925 model). And the absorbance spectra of the solutions were acquired at room temperature using a UV-Vis spectrophotometer (Jasco V-730 model). These techniques make it possible to identify the presence of the chemical elements that compose the C- steel in the solution and on the metal surface to assess the degree of corrosion. Optical microscopy (OM) was used to examine the immersion corrosion of carbon steel specimens in acidic solutions with and without inhibitors. The samples were sent to OM studies after the corrosion testing to determine the surface morphology.

3. Results and Discussion

3.1. Gravimetric measurements.

The influences of adding algae extract (FS) on the corrosion protection of carbon steel in 1M HCl solution were obtained by the mass loss method at 303 K after 6 hours of immersion. The corrosion rate (V) plus the inhibition efficiency IE(%) were measured by equations 1 and 2[16-19]:

$$\nu = \frac{\Delta m}{S \times t} \tag{1}$$

$$IE(\%) = \frac{v^{0} - v}{v^{0}} \times 100$$
(2)

where, Δm is the mass loss (mg), t is the immersion time (hours), S is the sample area (cm²), where v^0 is the corrosion rate in the hydrochloric acid solution (1M HCl), and v is the corrosion rate in the hydrochloric acid solution (1M HCl) with the inhibitor (mg cm⁻² h⁻¹).

The results reached are presented in Table 1. The efficiency increases up to 86% at 0.50 g/L. Moreover, the results reveal that improving the concentration of the FS extract decreases

the corrosion rate values. This decrease may be related to the characterization of the inhibitor, which affects the activity of the metal surface.

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C (g/L)	0	0.05	0.1	0.3	0.5		
$V ({\rm mg}{\rm cm}^{-2}{\rm h}^{-1})$	2.40	0.96	0.72	0.47	0.34		
IE (%)		60	70	80	86		
θ		0.60	0.70	0.80	0.86		

Table 1. The corrosion rate of metal and inhibition efficiency of FS extract in 1M HCl at 303 K.

According to the literature [20], the formation of corrosion products such as rust on the metal surface can improve the corrosion process. In addition to this, the presence of aggressive ions like Cl⁻ also accelerates the corrosion rate of the metal. Still, the use of this inhibitor makes it possible to decrease the destructive attack of this ion. In addition, the results obtained indicate that the mobilization of the inhibiting constituents towards the metal surface decreases the corrosion process, which may alter the formation of corrosion products. This effect can be explained by different approaches. The chemical species that form the SF extract can cover the metal surface, blocking the cathodic and anodic reactions or depreciating the chemical species' reduction and oxidation [21]. Concerning the inhibition efficiency, several kinds of research on green corrosion inhibitors from plant extract have been reported 94.8 % at 10 g/L for *Xanthium strumarium* extract [22], 88 % at 0.8 g/L for Glycyrrhiza glabra leaves extract [23], and 98% at 0.4 g/L for Sunflower seed hull extract [24]. Considering the result of this study, the inhibition efficiency of 86% at 0.5 g/L may favor the use of this extract as a corrosion inhibitor.

3.2. Potentiodynamic polarization measurements.

The FS extract was used to investigate its effect on the electrochemical behavior of carbon steel in 1M HCl solution at 303K by the potentiodynamic polarization measurements, as shown in Figure 1.



Figure 1. The effect of FS extract on the electrochemical behavior of carbon steel in 1M HCl solution at 303K.

The kinetic parameters, in particular the corrosion current density (i_{corr}), the cathodic and anodic slopes of Tafel (β_c , β_a), as well as the corrosion potential (E_{corr}) are summarized in Table 2. i_{corr} values are determined by Tafel extrapolation and are exploited to estimate the efficiency of inhibition IE_{Tafel} (%) (Equation 3)[25–27]:

$$IE_{Tafel}\left(\%\right) = \frac{i_{corr}^{0} - i_{corr}}{i_{corr}^{0}} \times 100 \tag{3}$$

where, i_{corr}^0 is the corrosion current density in the hydrochloric acid solution (1M HCl), and i_{corr} is the corrosion current density in the hydrochloric acid solution (1M HCl) with the inhibitor.

Conc.	$-E_{corr}$	i _{corr}	β_{a}	-β _c	$IE_{Tafel}(\%)$
(g/L)	(mV/SCE)	$(\mu A/cm^2)$	(mV/dec)	(mV/dec)	
0.0	477	430.9	111.0	118.6	-
0.5	455	58.9	49.0	108.3	86
0.3	458	65.0	53.0	131.9	85
0.1	483	99.4	76.2	115.0	77
0.05	435	135.1	60.8	106.2	69

Table 2. Electrochemical parameters and corrosion inhibition efficiency of carbon steel in 1M HCl, without and with the addition of different concentrations of SF extract at 303K.

Besides, the current density decreases with increasing concentration (Table 2), which confirms the creation of a protective layer that preserved the metal surface [28]. This appeared on the inhibition efficiency, which reached the percentage of 86%, close to the value of the gravimetric measurements. Furthermore, the cathodic and anodic slopes of Tafel (β_c , β_a) are changed with the addition of FS extract. In general, the Tafel slope value of the anode is more changed and significantly decreased, which is evidence that the oxidation reaction mechanism of iron is influenced. On the other hand, The Tafel slope value of the cathode is not more changed and stayed at the value of about 120 mV, which means that the compounds responsible for inhibition are not changed the mechanism of cathodic hydrogen evolution, which occurs for one electron in the charge transfer controlled reaction [29], and rather the adsorbed compounds block the active sites [30].

Therefore, the E_{corr} values are slightly shifted towards the anodic potential. According to the literature [31–34], the inhibitor can recognize it as an anodic inhibitor, cathodic inhibitor, or mixed inhibitor, depending on the variation of the corrosion potential. Therefore, in our case, the FS extract behaves like a mixed inhibitor since this change does not exceed ± 85 mV.

3.3. Electrochemical impedance spectroscopy (EIS).

The carbon steel impedance spectra in 1M HCl using different concentrations of FS extract are presented as Nyquist curves (Figure 2). Nyquist diagrams contain incomplete halfcircles representing the capacitive loop and having a center below the real axis.



Figure 2. Carbon steel impedance spectra in 1 M HCl solution, with modification of FS extract concentrations at 303 K.

The EIS results are generated by software through the electrical circuit illustrated in Figure 3 to model the studied electrochemical system and estimate numerical values matching the properties of the system[35,36]. In the equivalent electrical circuit, R_s is the resistance of the solution, R_p is the polarization resistance, and CPE represents the constant phase element that models the imperfect of the double layer.



Figure 3. Simulated carbon steel/electrolyte system using this electrical circuit.

The impedance behavior of CPE is calculated by this function [30,37]:

$$Z_{CPE} = \frac{1}{Y_0 \times (j \times \omega)^n} \tag{4}$$

 ω is the angular frequency,n and Y_o represent the phase shift and the magnitude of CPE, respectively.

And the double layer capacitance is measured via the CPE magnitude and the polarization resistance R_p , and the phase shift n (Equation 5) [30,37]:

$$C_{dl} = \left[Y_0^{1/n} \times \left(R_p\right)^{\frac{1-n}{n}}\right]$$
(5)

The following equation 6 represents the relation between the inhibition efficiency and the polarization resistance values [38–40]:

$$IE_{R_p}\left(\%\right) = \frac{R_p - R_p^0}{R_p} \times 100 \tag{6}$$

where, R_p^0 and R_p are the polarization resistance in the non-attendance and the attendance of the inhibitor, respectively. The values of the extracted impedance components are registered in Table 3.

 Table 3. Values of the extracted impedance components in 1 M HCl solution, with modification of FS extract concentrations at 303 K.

Conc. (g/L)	$\frac{\mathbf{R}_{\mathbf{s}}}{(\Omega \ \mathbf{cm}^2)}$	$\begin{array}{c} Y_0 (\times 10^4) \\ (\Omega^{-1} s^n cm^{-2}) \end{array}$	n	R _p (Ω cm ²)	C _{dl} (µF/cm ²)	IE_{R_p} (%)
blank	0.58	4.59	0.864	20.3	221.1	-
0.5	1.27	1.24	0.848	161.9	61.8	87
0.3	3.10	1.21	0.884	119.5	69.7	82
0.1	3.57	1.35	0.869	75.8	68.1	72
0.05	2.49	2.69	0.897	51.4	165.1	61

According to the results obtained (Table 3), it is observed that the concentrations of FS extract are proportional to the inhibition efficiency implies that the extract serves to protect the metal surface [2]. This protection is generally enhanced with the (n) parameter that reflects the inhomogeneity of the surface, which means that the metal surface is relatively homogeneous in the presence of FS extract compared to without it. This modification may reinforce the polarization resistance R_p values and decreases the bilayer capacitance C_{dl} . But the proportionality doesn't verify, which suggests that other parameters influence the polarization resistance R_p rises

from 20.3 Ω cm² to 161.9 Ω cm² and the bilayer capacitance C_{dl} decreases from 221.1 μ F/cm² to 61.8 μ F/cm², the variation of this value can be associated with the thickness evolution of the electrical double-layer [41], which is consistent with the Helmholtz model, assumed through the following equation 7 [42]:

$$C_{dl} = \frac{\varepsilon_0 \varepsilon}{d} S \tag{7}$$

where ε_0 denotes the permittivity in a vacuum, ε is the permittivity, d denotes film thickness, and S denotes surface area. From this relation, it is clear that the protection of the metal surface may be due to a decrease in the permittivity or an increase of the FS compounds thickness that adsorbed on the metal surface.

3.4. Temperature effect.

The estimated effect of temperature on the FS extract inhibition and the activation parameters of the metal applying the polarization measurements are studied in the presence of the inhibitor (0.5 g/L) and the range temperature 303 K-333 K (Figure 4).



Figure 4. The effect of temperature on the electrochemical behavior of the metal in 1 M HCl + 0.50 g/L of FS extract.

Table 4. The effect of temperature on the electrochemical parameters of the metal in 1 M HCl + 0.50 g/L of FS

extract.						
	Т (К)	-E _{corr} (mV/SCE)	i _{corr} (mA/cm ²)	β _a (mV/dec)	-β _c (mV/dec)	IE _{Tafel} (%)
	303	477	0.430	111.0	118.6	-
Blank	313	482	0.966	91.0	73.8	-
	323	458	1.509	87.2	87.6	-
	333	480	1.966	110.9	94.1	-
	303	455	0.058	49.0	108.3	86
FS	313	473	0.149	69.3	108.8	85
	323	434	0.778	60.4	126.8	60
	333	465	1.122	102.9	75.1	43

Analysis of the results grouped in Table 4 unveils that an augment in temperature improves the corrosion current density of the metal. But the effect is less in the presence of FS extract, which decreases the inhibition efficiency. This comportment may be elucidated through the desorption of FS extract molecules at higher temperatures due to weak interactions between the metal surface and the molecules responsible for the inhibition [43].

For the thermodynamic activation parameters, the corrosion rate as a function of temperature was studied, first using the Arrhenius equation 8 [44]:

$$i_{corr} = k \times \exp\left(\frac{-E_a}{R \times T}\right) \tag{8}$$

 i_{corr} is the density of the corrosion current, K is a pre-exponential factor, E_a is the activation energy and, R is the perfect gas constant, T is the absolute temperature.

Figure 5 illustrates the modification of the corrosion current density by the inverse of the temperature. Without and with inhibitor, this variation represents a straight line, and from the Arrhenius relation, we can calculate the activation energy.



Figure 5. Modifications of Arrhenius curves for C-steel, without (Blank) and with 0.50 g/L of FS extract in 1 M HCl.

Moreover, to understand the adsorption mechanism, the thermodynamic parameters of the dissolution of carbon steel in 1M HCl are examined without and with an optimal concentration of FS extract (Figure 6). In this regard, the transition state equation is used applying equation 9 [45–47]:

$$i_{corr} = \frac{R \times T}{N \times h} \times \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{R \times T}\right)$$
(9)

h: Plank constant, N: Avogadro number, ΔH_a Activation enthalpy, and ΔS_a : Activation entropy.

The variation of ln (i_{corr} / T) as a function of the inverse of the temperature 1/T is a straight line (Figure 7), with a slope equal to $(-\Delta H_a/R)$ and ordinate at the origin equal to (ln R/Nh + $\Delta S_a/R$). These parameters have been calculated and listed in Table 5.



Figure 6. Modification of the transition state curves for C-steel, without (Blank) and with 0.50 g/L of FS extract in 1 M HCl.

Table 5. Activation energies, enthalpies, and entropy values for C- steel in 1M HCl in the absence and thepresence of 0.5 g/L of the inhibitor.

Activation parameters	Ea (k.I/mol)	ΔH_a	ΔS_a
	(110/11101)	(kJ/mol)	(J/mol K)
Blank	41.92	39.27	-64.10
0.5 g/L	87.54	84.47	67.59

Moreover, Table 5 unveiled that the presence of FS extract in the corrosive solution improves the E_a that means the energy barrier for corrosion reaction is increased, which means the chemical compounds of FS extract enhance the protection of metal surface from the dissolution process. Besides that, the thermodynamic parameter ΔH_a with FS extract is greater (84.47 kJ mol⁻¹) than in the absence of inhibitor (39.27 kJ mol⁻¹), proposing that the decomposition of steel is delayed in the presence of FS extract [48]. The positive sign ΔH_a reflects the endothermic nature of the dissolution process of steel. The increase in ΔS_a is commonly described as an improvement in disorder caused by the substitution of water molecules by adsorption of FS extract chemicals onto the steel surface[49].

3.5. Adsorption isotherm.

The weight loss measurement was used to evaluate the nature of the adsorption of FS inhibitor on the carbon steel surface in 1 M HCl solution at 303 K. The corrosion inhibition efficiencies (η) of the selected method was used to evaluate the surface coverage (θ) as $\theta = \eta/100$ (Table 1) in the monolayer adsorption model of Langmuir isotherm expression presented as Eq. (10).

$$Conc. / \theta = 1 / K_{ads} + Conc.$$
⁽¹⁰⁾

where K_{ads} is the adsorption constant and Conc. is the concentration of the corresponding FS on the carbon steel surface.

The plot of the ratio of the FS inhibitor concentration and the surface coverage $(Conc./\theta)$ versus concentration (Conc.) were used to generate the Langmuir isotherm curves for the FS inhibitor shown in Figure 7. The adsorption constant (K_{ads}), slope, and other

Langmuir isotherm parameters are enumerated in Table 6. It can be observed that the slope obtained from the weight loss method for FS is approximately following the monolayer adsorption model proposed in Eq. (10). This can be interpreted that the adsorption of FS inhibitor on the surface of carbon steel in 1 M HCl solution at 303 K obeys a monolayer adsorption model. The K_{ads} value is attributed to measuring the affinity of an inhibitor to the adsorption site; usually, a high value suggests protection of the metal surface. In our case, the value is less related to the nature of FS extract, which contains numerous chemical compounds, which let difficult to estimate the molar concentration. As electrochemical and gravimetric methods verified the efficacy, we can suggest that FS extract compounds follow Langmuir isotherm with an adsorption interaction with carbon steel.



Figure 7. Langmuir isotherm curves of carbon steel surface in 1 M HCl solution in the absence and presence of different concentrations of FS inhibitor at 303 K.

In order to determine the nature of the interaction, physisorption or chemisorption, between the molecules that compose the FS extract and the metal surface, Gibb's free energy of adsorption (ΔG_{ads}°) must be estimated using Eq. (11).

$$\Delta G_{ads}^{\circ} = -R \times T \times Ln \Big(C_{H_2O} \times K_{ads} \Big) \tag{11}$$

The parameters R, C_{H2O} , and T are universal gas constant, the concentration of pure water in the solution, and temperature (K), respectively (R = 8.314 J mol⁻¹ K⁻¹ and $C_{H2O} = 10^3$ g/L). However, it could be mentioned that FS extract weight is not recognized. Thus, ΔG_{ads}^{o} determination is not allowed, which confirms what has been described previously using other plants that have been extracted with different solvent and extraction techniques so that to obtain green corrosion inhibitors [50–53].

Table 6. Langmuir isotherm parameters of carbon steel surface in 1 M HCl solution in the presence of FS inhibitor at 303 K.



3.6. UV–Vis–NIR spectroscopy.

UV-Vis-NIR diffuse reflectance spectroscopy of the surface was analyzed after the 48 hours immersion time at room temperature. As shown in Figure 8, the reflectance of the metal https://biointerfaceresearch.com/ 7084

surface after immersion in the presence of FS extract shows a percentage of reflectance between that presented by the blank solution and before immersion.



Figure 8. UV-Vis-NIR diffuse reflectance spectroscopy of the surface for C-steel before and after the 48 hours immersion time in 1 M HCl (Blank) and with 0.50 g/L of FS extract at room temperature.



Figure 9. Second derivatives of K-M function spectra of the surface for C-steel before and after the 48 hours immersion time in 1 M HCl (Blank) and with 0.50 g/L of FS extract at room temperature.

Furthermore, we also examined the second derivatives of K-M (Kubelka-Munk) function spectra to identify the iron oxides [54]. Figure 9 shows the possibility of detecting the absorption bands corresponding to hematite (Hm), Magnetite (Mt), and Goethite (Gt), Maghemite (Mm), Lepidocrocite (Lp), δ -FeOOH[54–57]. However, These oxides have overlapping bands that are difficult to differentiate.

For this, From the point of view of the degradation of a material, the amplitude between the lowest point and the highest near point of the absorption bands can be accepted as a quantitative parameter to estimate the degree of degradation or protection of material against an aggressive environment [37,58,59]. In the case of FS extract, the amplitude of the iron oxides corresponding to the surface of the metal shows an amplitude between that presented by the blank solution and before immersion, which means that the surface was less attacked and protected.

For further interpretation of the inhibition effect, UV–Vis Spectroscopy of the solution was utilized. Figure 10 displays the UV–Vis Spectroscopy of the solution after immersion of the metal for 2 days (48h), the black line corresponds to the 1M HCl solution (Blank), and the green line linked to the 1M HCl solution with 0.5 g/L of the inhibitor (FS).



Figure 10. UV-Vis absorption spectroscopy of the 1 M HCl solution (Blank) and with 0.50 g/L of FS extract after 48 hours of immersion time of C-steel at room temperature.

As observed in Figure 10, a peak at 334 nm is detected in the blank solution, and this band is related to the presence of ferric chloride FeCl₃ [60]. Usually, the dissolution of bare iron in the hydrochloric solution is a transformation of Fe atom into ferrous ions Fe^{2+} , the presence of ferric ions, in this case, can be related to the dissolution of iron oxides that contain ferric ions in their structure (Equation 12-13).

$$Fe_2O_{3(s)} + 6HCl_{(aq)} \rightarrow 2FeCl_{3(aq)} + 3H_2O_{(L)}$$

$$\tag{12}$$

$$Fe_{3}O_{4(s)} + 8HCl_{(aq)} \rightarrow FeCl_{2(aq)} + 2FeCl_{3(aq)} + 4H_{2}O_{(L)}$$

$$\tag{13}$$

In addition, this is confirmed by the previous technique, which is identified the iron oxides that have Fe^{3+} . Another suggestion that can enhance the presence of $FeCl_3$ is the oxidation process of ferrous chloride $FeCl_2$ with oxygen, as demonstrated by the following reaction:

$$4FeCl_{2(aq)} + O_2 + 4HCl_{(aq)} \to 4FeCl_{3(aq)} + 2H_2O_{(L)}$$
(14)

On the other hand, the absence of this peak is observed in the solution with the inhibitor, it is a sign of the inhibitory effect of the SF extract, which delays the dissolution of the bare metal of iron to the ferrous ions.

3.7. Optical morphology.

To confirm the inhibitory effect of the FS extract on the metal, the surface morphology was inspected by optical microscopy after 48h of immersion in 1 M HCl with and without the FS extract (Figure 11). Figure 11-b shows serious damage to the metal surface due to an aggressive environment caused by Cl^{-} ion activity. In contrast, the existence of 0.5 g/L of FS attenuates the aggressivity of HCL molecules, as shown in Figure 11-c.



Figure 11. Optical morphology of the carbon steel surface after 48h of immersion at room temperature. (a) before immersion, (b) in 1 M HCl, (c) in 1 M HCl + 0.5 g/L of FS.

4. Conclusions

In this study, the gravimetric measurements of carbon steel explained that *Fucus* spiralis (FS) extract is a novel corrosion inhibitor in an aggressive environment of 1 M HCl at 303 K, with an efficiency of 86 % at 0.5 g/L. Polarization studies have clarified that the inhibitor acts as a mixed inhibitor which influences the anodic reaction mechanism and just blocks the active cathodic sites. This decreases the corrosion current density and shifts the E_{corr} slightly. Moreover, This change was verified by EIS graphs, in which the FS extract improves the resistance of the polarization (R_p) and minimizes the double layer capacity (C_{dl}) of carbon steel. Temperature affected the performance of the FS extract due to weak interactions between the metal surface and the chemical substances responsible for the inhibition, assuming that the adsorption is mainly due to the physisorption mechanism. Thermodynamic parameters explained that the FS extract in the aggressive solution enhances the activation energy, retains the endothermic process of the reactions at the metal/solution interface, and increases the level of disorder. Besides that, the adsorption isotherm method showed that FS extract follows Langmuir isotherm. The results acquired were homogeneous with the results obtained by UV-Vis-NIR spectroscopy, which is shown a decrease of iron oxides of the metal surface and a diminution of iron ions in the solution, especially that optical morphology showed that FS extract attenuates the aggressivity of HCl.

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Conflicts of Interest

The authors declare no conflict of interest.

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