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# Gracilaria bursa-pastoris as eco-friendly corrosion inhibitor for mild steel in 1 M HCl media

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## ABSTRACT

*This work describes the successful performance of Gracilaria bursa-pastoris as an eco-friendly corrosion inhibitor for mild steel in HCl 1M solution. This study investigated by weight loss measurement, electrochemical impedance spectroscopy (EIS) and Tafel polarization. The inhibition mechanism is discussed considering thermodynamics of adsorption and kinetics of the electrochemical reactions. Gracilaria bursa-pastoris is a mixed-type inhibitor and the mode of inhibition results from the geometric blocking effect of physisorbed inhibitive species at the metal surface.*

**Key words:** Mild steel, Gracilaria bursa-pastoris, Plant, HCl, Corrosion, Green inhibitor.

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## INTRODUCTION

These days, studies of steel corrosion phenomena have become an academic and industrial subject, especially in acid media [1]. More recently, much effort has been devoted to the development of the so-called green corrosion inhibitors that are defined to be more eco-friendly than the majority of the currently applied organic compounds [2]. Currently, research in corrosion is focused on ''green corrosion inhibitors'', that show good inhibition efficiency with low risk of environmental pollution [3]. The term ''green inhibitor'' or ''ecofriendly inhibitor'' refers to substances that are biocompatible such as plant extracts since they are of biological origin [4- 6]. Thus natural products (derived from plant materials) are being studied for their corrosion inhibition potential as they are showing good corrosion protection and are more environment friendly [5–6]. We have successfully reported many green corrosion inhibitors for metals in acid media from various plant sources [7].

Some investigations have in recent times been made into the corrosion inhibiting properties of natural products of plant origin, and some natural products have been found to generally exhibit good inhibition efficiencies [8]. The significance of this area of research is primarily due to the fact that natural products are environmentally friendly and ecologically acceptable. The yield of these natural products as well as the corrosion inhibition abilities of the plant extracts vary widely depending on the part of the plant [9] and its location [10]. One compound effective in a certain medium with a given metal may be ineffective for the same metal in another medium [11]. Gracilaria bursa-pastoris is a red algal species. It is broadly distributed in the lagoon of Nador in the Mediterranean Moroccan costs. It contained a high total phenolic content, vitamin E, vitamin C and the antioxidant capacity. It can be utilized as a source of natural antioxidant molecules and could be useful for food industry [12] and as a biofilter of nutrients [13].

To the best of our knowledge, there is no previous report on the study of the corrosion inhibitive effect of Gracilaria bursa-pastoris extract.

The objective of this work is to study the influence of Gracilaria bursa-pastoris on the corrosion of mild steel in 1M HCl acid medium at different concentrations of inhibitor by electrochemical measurements: weight loss, polarization curve and electrochemical impedance spectroscopy.

## MATERIALS AND METHODS

### 2.1. Solutions and samples preparation:

Corrosion experiments were performed on mild steel specimens (Coupons were cut into 1.5× 1.5 × 0.05 cm3 dimensions) with weight percentage composition as follows: (0.09% P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S and Fe balance). Specimens were wet-ground using emery paper from grade 400 to 1200; rinsed with distilled water, degreased with acetone and dried with warm air before use.

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. Reed algae Gracilaria bursa-pastoris was collected from Nador lagoon (Figure 1) in May 2015. The algal species was identified by Professor N. Elkhiati (Faculty of Sciences Ain Chock, seaweed group, Casablanca, Morocco).

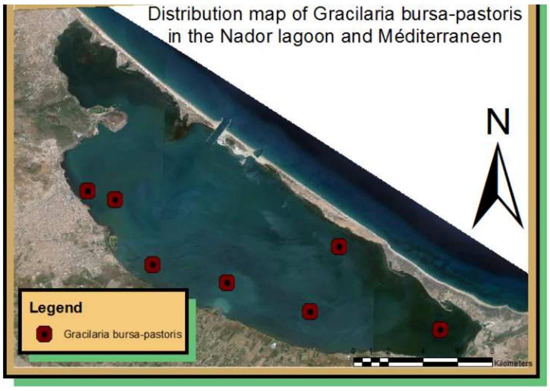

**Figure 1: sampled from Nador lagoon in Mediterranean Moroccan costs**

In the laboratory, the algae was carefully cleaned, washed several times with tap water, distilled water, then dried at 40°C, ground and kept in dark. Different inhibitor concentrations (0.125, 0.25, 0.5 and 1 g/l) were prepared from the algae powder by dissolving the required amount of Gracilaria bursa-pastoris in 100 mL of 1 M HCl with stirring at room temperature. 100 mL of 1 M HCl without inhibitor was used as blank test solution.

**(a)** **(b)**

**Figure 2: Gracilaria bursa-pastoris, a) plant, b) powder**

### 2.2. Gravimetric measurements:

Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 100 $cm^3$. The immersion time for the weight loss is 6 h at (308±1) K. In order to get good reproducibility, experiments were carried out in duplicate. The average weight loss was obtained. The corrosion rate (v) is calculated using the following equation:

$$v = \frac{w}{st} \qquad (1)$$

Where: w is the average weight loss, S the total area, and t is immersion time. With the corrosion rate calculated, the inhibition efficiency (Ew) is determined as follows:

$$Ew\,\% = \frac{V0 - V}{V0} X\,100 \qquad (2)$$

Where:  V0 and V are, respectively, the values of corrosion rate with and without inhibitor

**2.3. Electrochemical measurements:**

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Volta master soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from −800 mV to −200 mV at 308 K. The solution test is there after de-aerated by bubbling nitrogen. Inhibition efficiency (Ep%) is defined as Equation (3), where icor(0) and icor(inh) represent corrosion current density values without and with inhibitor, respectively.

$$Ep\% = \frac{\mathrm{icor(0)} - \mathrm{icor(inh)}}{\mathrm{icor(0)}} \mathrm{x}\,100 \qquad (3)$$

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at Ecor after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation.  Inhibition efficiency (ER%) is estimated using the relation(4), where Rt(0) and Rt(inh) are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

$$ER\% = \frac{\mathrm{Rt(inh)} - \mathrm{Rt(0)}}{\mathrm{Rt(inh)}} \mathrm{x}\,100 \qquad (4)$$

## RESULTS AND DISCUSSION

### 3.1. Weight Loss Measurements:

### 3.1.1. Effect of inhibitor concentration:

The corrosion rate (v) and the inhibition efficiency, Ew(%), values obtained from weight loss method at different concentrations of Gracilaria bursa-pastoris after 6 h of immersion in 1 M HCl at 308C were given in Table 1. It is obvious from these results that along with the increase of the inhibitor concentration, the values of $v$ decreases gradually, i.e. the corrosion of steel was retarded by Gracilaria bursa-pastoris, or the inhibition was enhanced by the inhibitor concentration. Indeed, the variation in Ew with concentration of inhibitor, presented in Figure 3, showed that the protection inhibition efficiency increased with the increase of the inhibitor concentration. The maximum Ew(%) of 98% was achieved at 1g/l after 6 h of immersion in 1 M HCl. Noticeably, when the concentration of Gracilaria bursa-pastoris was less than 0.5g/l, Ew increased sharply with an increase in concentration, but a further raise inhibitor concentration caused no appreciable change in inhibitive performance. This behavior can be due to the fact that the adsorption coverage of inhibitor on steel surface increases with the inhibitor concentration.

**Table 1. Corrosion parameters obtained from weight loss measurements for carbon steel in 1 M HCl containing various concentrations of Gracilaria bursa-pastoris at 308 K**

| Inhibitor | Concentration (g/l) | *V* (mg cm$^{-2}$ h$^{-1}$) | E*w* (%) |
|---|---|---|---|
| 1M HCl | - | 8.82 | -- |
| *Gracilaria bursa-pastoris* | 1 | 0.02 | **98** |
| | 0.5 | 0.06 | 93 |
| | 0.25 | 0.09 | 89 |
| | 0.125 | 0.10 | 88 |

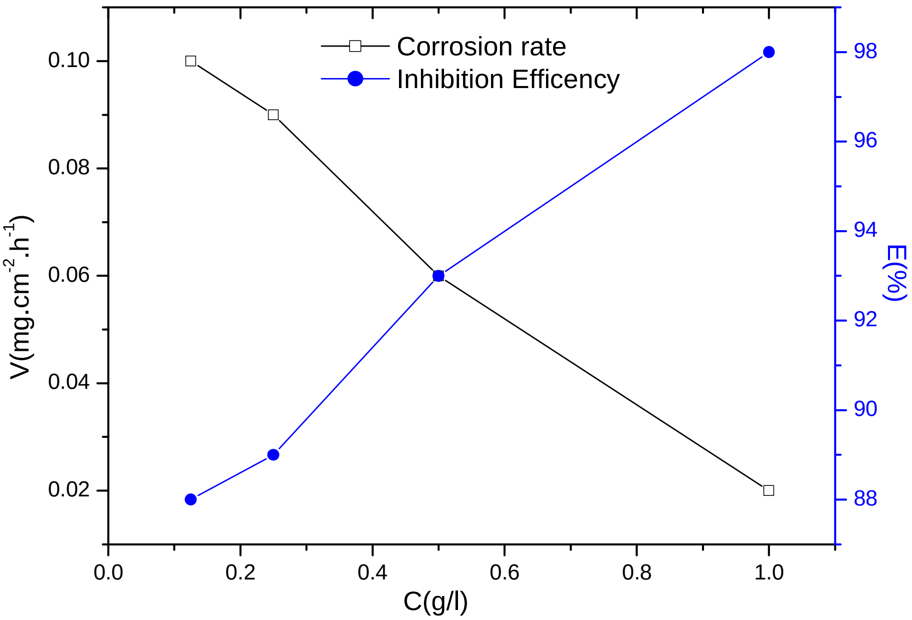

**Figure 3. Relationship between corrosion rate and corrosion inhibition efficiency of mild steel in 1 M HCl and concentration of Gracilaria bursa-pastoris**

### 3.2. Electrochemical impedance spectroscopy (EIS).

EIS experiments were undertaken mainly, as an independent and complementary tool to determine corrosion rates in a rapid and accurate way. Additionally, EIS allowed to gain insight into kinetics of electrochemical processes and the inhibition mode which occur at the mild steel/1 M HCl interface modified by the presence of Gracilaria bursa-pastoris. Figure 4 shows impedance spectra as Nyquist plots that were obtained for mild steel in the absence and presence of different concentrations of Gracilaria bursa-pastoris.

The corrosion inhibitive efficiency of compound 1–0.125 (g/l) for mild steel electrodes in 1 M HCl was examined via electrochemical impedance spectroscopy and the obtained Nyquist plots are shown in Figure 4. The impedance diagrams for blank (without inhibitor) and those for 1– 0.125 feature a depressed semicircle (Figure 4), indicating that the corrosion process was mainly controlled by charge transfer and the presence of this compound did not change the mechanism of mild steel dissolution in HCl [14, 15].

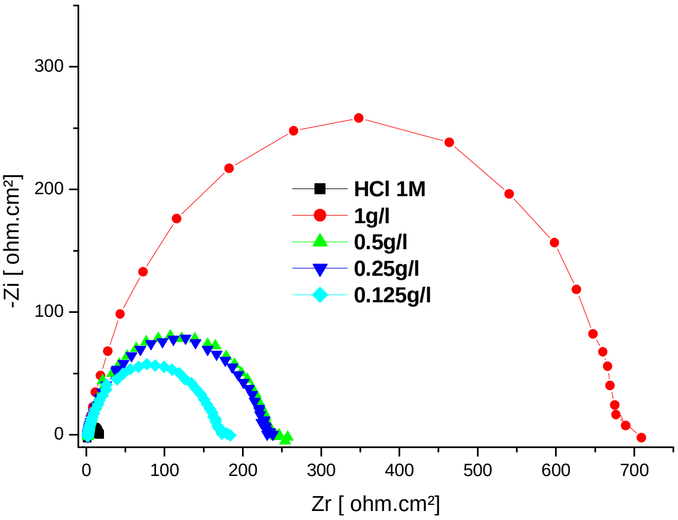

**Figure 4. Nyquist plots of mild steel in 1 M HCl without and with different concentrations of Gracilaria bursa-pastoris at 308 K**

Analysis of the Nyquist plots (Figure 4) showed a depressed capacitive loop which arises from the time constant of the electrical double layer and charge transfer resistance. This could be attributed to different physical phenomena such as roughness and in homogeneities of the solid surfaces, impurities, grain boundaries and distribution of the surface active sites [16]. All the curves obtained are approximated by a single capacitive semicircle, showing that the corrosion process was mainly charge-transfer controlled [17]. The general shape of the curves is very similar for all concentrations; the shape is maintained throughout the whole test period, indicating that almost no change in the corrosion mechanism occurred either due to the immersion time or to the inhibitor addition [18].

**Table 2. Impedance elements derived from spectra recorded for steel in 1 M HCl with varying concentrations of Gracilaria bursa-pastoris at (308 ± 1) K**

| Inhibitor | Concentration (g/l) | $R_{ct}$ ($\Omega.cm^2$) | $R_s$ ($\Omega.cm^2$) | $C_{dl}$ ($\mu f/cm^2$) | E (%) |
|---|---|---|---|---|---|
| 1M HCl | - | 14.57 | 1.37 | 200 | -- |
| *Gracilaria bursa-pastoris* | 1 | 683 | 1.88 | 58.25 | **97** |
|  | 0.5 | 232 | 1.67 | 69.81 | 94 |
|  | 0.25 | 227 | 1.71 | 77.18 | 93 |
|  | 0.125 | 164 | 1.81 | 86.31 | 91 |

From Table 2, it is observed that addition of inhibitor increases Rct values (14.57–683 Ω.cm2) while decreases Cdl values (200–86.31µf/cm2); which indicated reduction in corrosion rate. Correspondingly, studied inhibitor showed good E(%) with similar trend and reached maximum of above 97% at concentration level of 1g/l.

Figure 5 show a typical set of impedance diagrams for mild steel in 1 M HCl without and with various concentrations of Gracilaria bursa-pastoris. The Nyquist diagram in the absence of inhibitor shows only one depressed capacitive loop at the higher frequency range (HF) with one capacitive time constant in the Bode-phase plot (Figure 5). In this case, the standard Randles circuit model of Figure 6, which has been previously used [19], fits well our experimental results. In this equivalent circuit, Rs is the solution resistance, Rct present the charge transfer resistance and CPE is the constant phase element. The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor in order to take into account the electrode surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [20, 21] and therefore to give a more accurate fit [22].

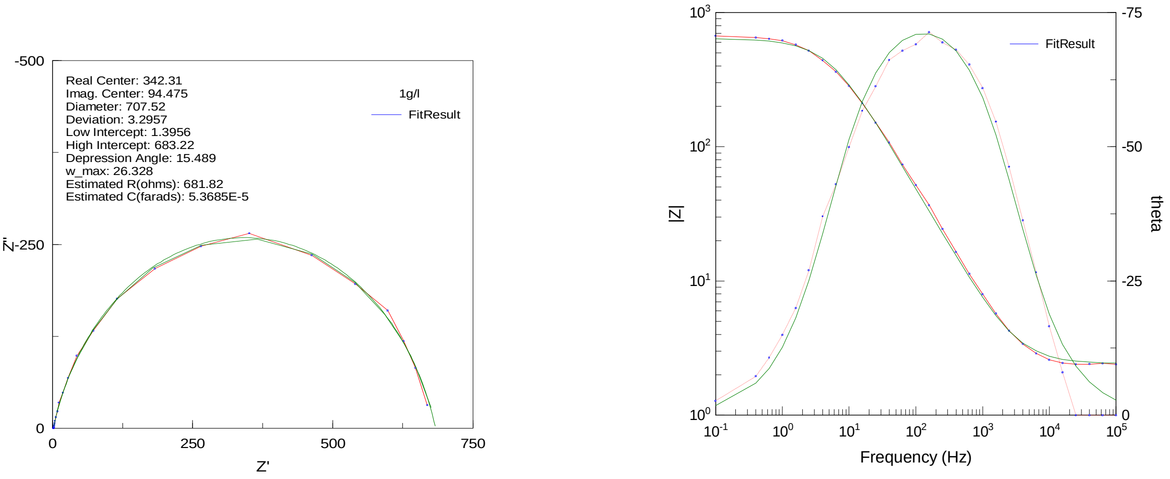

**Figure 5. Experimental data and best-fit results for impedance spectra (plotted as Nyquist and Bode diagrams) for steel in 1 M HCl containing 1.0 g/l of *Gracilaria bursa-pastoris***

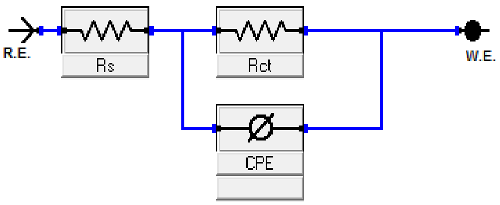

**Figure 6. Equivalent circuit used to fit the electrochemical impedance data**

### 3.3. Potentiodynamic polarization study

Figure 7 displays the potentiodynamic polarization curves of mild steel in 1 M HCl medium which were obtained before and after the introduction of various doses of Gracilaria bursa-pastoris inhibitor. Various corrosion parameters viz., corrosion current density (icorr), corrosion potential (Ecorr) and Tafel slope value (βa) derived from these figure are given in Table 3. The corrosion current densities were estimated by Tafel extrapolation of the cathodic and anodic curves to the open circuit corrosion potential.

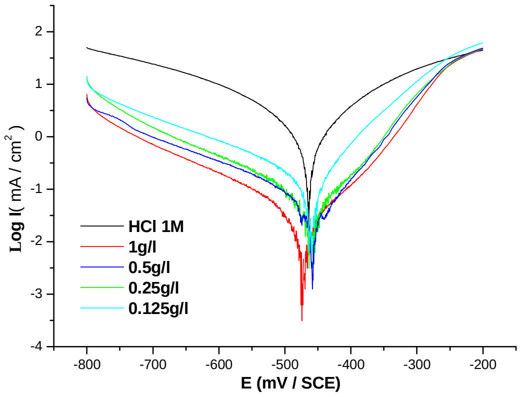

**Figure 7. Tafel plots for mild steel in 1 M HCl medium in presence and absence of *Gracilaria bursa-pastoris***

**Table 3: Polarization parameters for the mild steel in 1 M HCl containing different concentrations of *Gracilaria bursa-pastoris***

| Inhibitor | Concentration (g/l) | -$E_{corr}$ (mV/SCE) | $I_{corr}$ ($\mu A/cm^2$) | -βc | βa | E (%) |
|---|---|---|---|---|---|---|
| ***1M HCl*** | - | 464 | 1386 | 164 | 135 | -- |
| ***Gracilaria bursa-pastoris*** | 1 | 456 | 48 | 172 | 74 | **97** |
| | 0.5 | 456 | 50 | 140 | 67 | 96 |
| | 0.25 | 446 | 68 | 131 | 67 | 95 |
| | 0.125 | 437 | 128 | 190 | 72 | 91 |

From this table, it can be concluded that:
→ The Icorr values decrease with increasing inhibitor concentration.
→ The values of inhibition efficiency (E %) increase with inhibitor concentration reaching a maximum value (97%) at 1 g /L.
→ The Gracilaria bursa-pastoris inhibitor is a mixed inhibitor.

On the other hand, the excellent behaviour of Gracilaria bursa-pastoris previously indicated in the Weight loss and EIS measurements is confirmed. Figure 8 gives the inhibition efficiency of Gracilaria bursa-pastoris in aggressive medium calculated by different methods.

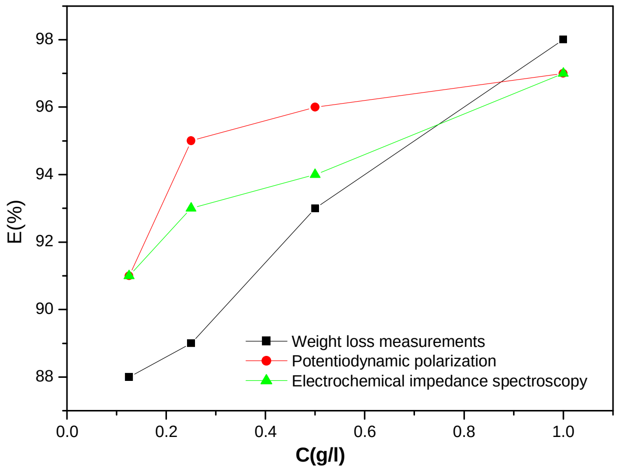

**Figure 8. Inhibition efficiency *vs* inhibitor concentrations calculated by different methods**

### 3.4 Adsorption Isotherm

Because the corrosion of metals is associated with a negative change in the Gibbs free energy, an absorption isotherm must be calculated for the system in order to obtain the adsorption free energy ($\Delta G°_{ads}$) values; this isotherm is very necessary for understanding the mechanism of corrosion inhibition. In order to do this, the adsorption behavior must be known. It was assumed that the adsorption of this inhibitor followed the Langmuir adsorption isotherm. The Langmuir adsorption isotherm, presented in Eq. (5), is most often used to calculate the equilibrium constant ($K_{ads}$). The value θ in Eq. (5) represents the degree of surface coverage obtained from the potentiodynamic data [23]. Figure 9 shows $C_{inh}/\theta$ vs. $C_{inh}$ and the straight line obtained for *Gracilaria bursa-pastoris*. The values of $\Delta G°_{ads}$ are obtained using Eq. (6). The values of the intercept are used to calculate $K_{ads}$. Table 4 shows the calculated values of $K_{ads}$ and $\Delta G°_{ads}$.

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (5)$$

$$\Delta G°_{ads} = -RT.\ln(55,5.K) \qquad (6)$$

In general, for values of $\Delta G°_{ads}$ up to -20 kJ mol$^{-1}$, the adsorption types were regarded as physisorption, where the inhibition occurs due to the electrostatic interactions between the charged molecules and the charged metal. For $\Delta G°_{ads}$ values of -40 kJ mol$^{-1}$ or smaller were regarded as chemisorption, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form a covalent bond. Table 4 showed that the calculated values of were in the range of -19.51 kJ mol$^{-1}$. This suggested that the *Gracilaria bursa-pastoris* were adsorbed physically onto the mild steel surface [24, 25].

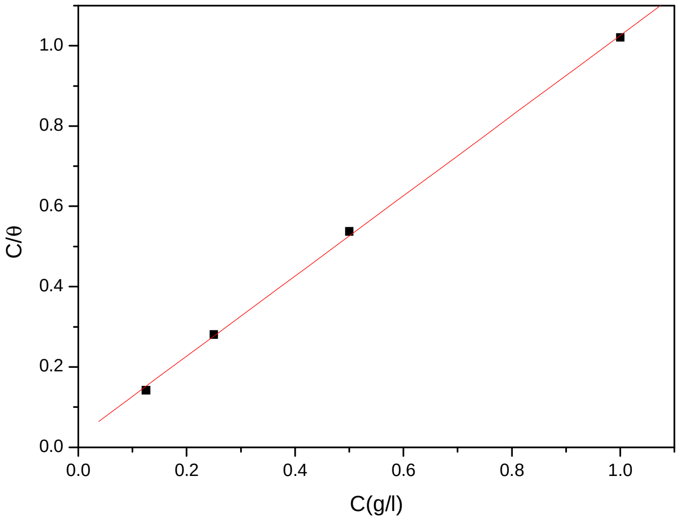

**Figure 9. Adsorption isotherms of Gracilaria bursa-pastoris on the mild steel surface in 1 M HCl**

**Table 4. Thermodynamics parameters adsorption of Gracilaria bursa-pastoris on the steel mild in HCl 1M media**

| Inhibitor | $K_{ads}$ | $\Delta G°_{ads}$ kJ mol$^{-1}$ | Linear coefficient regression (r) |
|---|---|---|---|
| *Gracilaria bursa-pastoris* | 36.87 | -19.51 | 0.999 |

## CONCLUSION

From the principal result of the present work we can conclude that:

- ✓ The data obtained from the Tafel polarization curves, electrochemical impedance spectroscopy (EIS) and Weight loss , approve that *Gracilaria bursa-pastoris* is effective corrosion inhibitors for mils steel in 1 M HCl.
- ✓ The Tafel polarization curves indicate that both *Gracilaria bursa-pastoris* is mixed anodic-cathodic type inhibitors.
- ✓ The adsorption of *Gracilaria bursa-pastoris* followed the Langmuir adsorption isotherm, and the adsorption mechanism of inhibitor on mild steel surface from 1 M HCl occurred physically.

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