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Caulerpa prolifera green algae using as eco-friendly corrosion inhibitor for mild steel in 1 M HCl media

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ABSTRACT

The marine macroalgae extract of caulerpa prolifera in aqueous 1 M HCl was systematically investigated to ascertain its inhibitor effect on corrosion of mild steel and its mechanism of the inhibition by electrochemical and weight loss methods. The results revealed a high inhibitive effect of C. prolifera. The inhibition efficiency was found to increase with increasing concentration of the algal extract but decreased with increase in temperature which is attributed to the physisorption. Potentiodynamic polarization measurement showed that C. prolifera extract acted as mixte type inhibitor. The increase in activation in energies of corrosion process in presence of the extract indicates that C. prolifera retarded the rate of corrosion of mild steel in 1 M HCl solution. The nature of adsorption of the C. prolifera on mild steel surface was in conformity with Langmuir isotherm. The results obtained with different method are in good agreement.

Keywords: Mild steel, C. Prolifera, HCl, Corrosion, Green inhibitor

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INTRODUCTION

Acid solutions are widely used in industry such as acid pickling, acid cleaning, or acid decaling procedures of metallic materials. Because of aggressive properties of acid solutions, inhibitors are commonly used to reduce corrosive attack of acids. Many synthetic compounds offer good anticorrosive action, but most of them being highly toxic to both human and environment (1-3). Thus the application of synthetic corrosion inhibitor should be replaced with natural inhibitor. In recent years, research into the use of low-cost and ecofriendly compounds as corrosion inhibitors for mild steel were intensified. Many researchers have studied the use of plant based inhibitor and the results shows that this new type of inhibitors is proven effectively to reduce the corrosion rate on the metal (4-12). In the literature, other researchers reported that the extracts of marine algae investigated as inhibitors of corrosion on metals in acid media (13,14) possessed excellent corrosion inhibitive effects.

The encouraging results obtained in our laboratory by naturally oils and extracts as corrosion inhibitors of steel in acid solutions permit to test more plants. *Caulerpa prolifera* Lamouroux is a marine alga, belonging to the Caulerpaceae family. It is broadly distributed in the Mediterranean Moroccan costs from Saidia to Tangier (Benhissoune and al, 2001) (15). Earlier studies had shown anti HSV-1 (16), antibacterial activity (17), antitumor activity (18) and plant regulatory effects (19) for caulerpin. Ahmed and col. (20) reported that C. prolifera methanolic extract played a vital role in ameliorating dyslipidemia and its complications particularly oxidative stress and inflammation. Recently, Sethuraman and Kamal (21) reported that extracts of marine algae viz., Caulerpa racemosa possessed a high corrosion inhibitive effect. To the best of our knowledge, there is no previous report on the study of the corrosion inhibitive effect of C. Prolifera extract. In the present study, we investigated the corrosion inhibition of C. Prolifera on carbon steel in 1 M HCl solution at different temperatures and concentrations and we elucidate the mechanism of inhibition. This study war realized by weight loss and electrochemical impedance spectroscopy (EIS) methods.

MATERIALS AND METHODS

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. Green alga *Caulerpa prolifera* Lamouroux (Caulerpaceae) was collected from Nador lagoon (Fig. 1) in October 2013, March and June 2014**.**

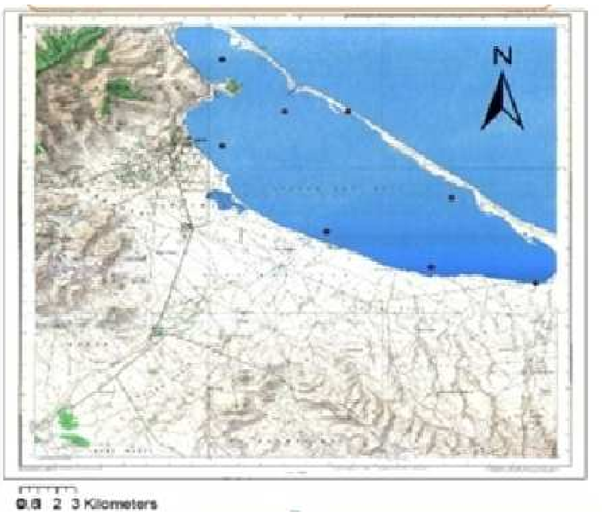

Figure 1: Caulerpa prolifera sampled from Nador lagoon in Mediterranean Moroccan costs

In the laboratory, the alga was carefully cleaned, washed several times with tap water, distilled water, then dried at 40°C, ground and kept in dark, labeled till use. Collected samples were determined by Pr. Elkhiati (University Hassan II, Morocco). Different concentrations (0.125, 0.25, 0.5 and 1 g/l) were prepared from the alga powder by dissolving the required amount of C. prolifera 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: Caulerpa prolifera, Family: Caulerpaceae, Order: Caulerpales, Genus: ***Caulerpa*****,, a) plant, b) powder**

Coupons were cut into 1.5× 1.5 × 0.05 cm^3 dimensions having composition (0.09%P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S and Fe balance) used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 400, 800, 1000, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 50 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 (E_w) is determined as follows:

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

Where: $\mathbf{V_0}$ and **V** are, respectively, the values of corrosion rate with and without inhibitor

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster 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 (E_p%) is defined as Equation (3), where icorr(0) and icorr(inh) represent corrosion current density values without and with inhibitor, respectively.

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

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at E_{corr} 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 (E_R%) is estimated using the relation(4), where $R_{t(0)}$ and $R_{t(inh)}$ are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

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

RESULTS AND DISCUSSION

3.1. Weight loss measurements

Values of the inhibition efficiency and corrosion rate obtained from the weight loss measurements of mild steel for different concentrations of C. prolifera in 1 M HCl at 308K after 6 h of immersion are given in table 1. The inhibition efficiency is defined as follows:

$$E_W\,\% = \frac{V_0 - V}{V_0} X\,100 \qquad (5)$$

Where: $\mathbf{V_0}$ and **V** are, respectively, the values of corrosion rate with and without inhibitor.

The analysis of these results (Figure 1) shows clearly that the corrosion rate decreases (W (mg/h.cm^2) while the inhibition efficiency (E_w %) increases with increasing inhibitor concentration reaching a maximum value of 96.34 % at a concentration of 1 g/l. This behavior can be attributed to the increase of the surface covered θ (E_w %/100), and that due to the adsorption of natural compounds on the surface of the metal, as the inhibitor concentration increases. We can conclude that C. prolifera is a good corrosion inhibitor for mild steel in 1 M HCl solution.

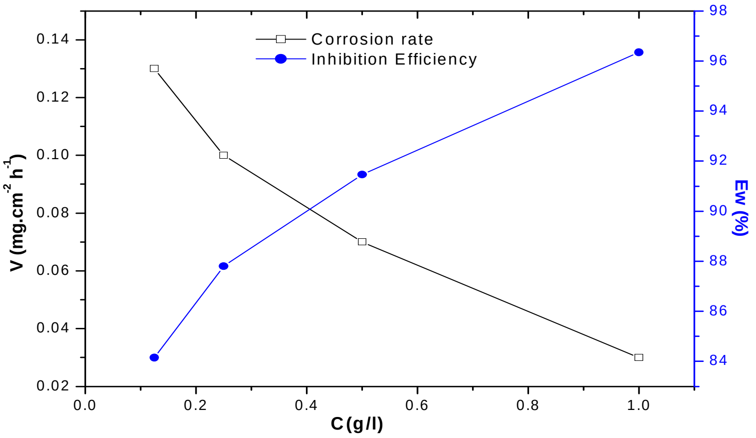

Figure 1. The corrosion rate and the inhibition efficiency E_w% for Mild steel in 1 M HCl containing different concentrations of C. prolifera

3.1.1. Effect of temperature

The effect of temperature on the inhibition efficiency, in the temperature range 308-353 K, in 1 M HCl, was studied using gravimetric experiments in the absence and presence of 1 g/l of inhibitor after 1 h of immersion time.

The fractional surface coverage Θ can be easily determined from weight loss measurements by the ratio E_w% / 100 if one assumes that the values of E_w% do no differ substantially from Θ. It is clear from Table 1 that increasing the corrosion rate (V) was more pronounced with the rise of temperature for blank solution. In the presence of the C. prolifera inhibitor, the corrosion rate of mild steel decreased at any given temperature as inhibitor concentration increased due to the increasing of the degree of surface coverage. The results obtained are summarized in Table 1.

Table 1.Effect of temperature on the corrosion rate of mild steel in 1 M HCl at different concentrations in the temperature range 308-333 K for 1 h

Temperature (K)	Inhibitor	V (mg/cm^2.h)	E (%)	Θ
308	HCl 1M	0.82	--	--
	C. prolifera	0.03	96.34	0.96
313	HCl 1M	1.69	--	--
	C. prolifera	0.11	93.49	0.93
323	HCl 1M	3.23	--	--
	C. prolifera	0.27	91.64	0.92
333	HCl 1M	6.73	--	--
	C. prolifera	0.67	90.04	0.90

In order to calculate activation parameters for the corrosion process, Arrhenius Eq. (6) and transition state Eq. (7) were used [22]:

$$V = \quad A\exp(\frac{-E_a}{RxT}) \qquad (6)$$

$$V = \frac{RxT}{Nxh}\exp(\frac{-\Delta S_a}{R})\exp(\frac{-\Delta H_a}{RxT}) \qquad (7)$$

Where *E*a is the apparent activation corrosion energy; *R* is the universal gas constant; *k* is the Arrhenius pre-exponential factor. *h*is Plank’s constant. *N* is Avogrado’s number. Δ*S*a is the entropy of activation and Δ*H*a is the enthalpy of activation.

Arrhenius plots for the corrosion rate of mild steel are given in Fig. 2 and Fig. 3. Values of apparent activation energy of corrosion (E_a) for mild steel in 1.0 M HCl with the absence and the presence of various concentrations of cababes were determined from the slope of Ln(v) versus 1/T plots C. prolifera extract and shown in Table 2. The value of 63.50 kJ mol^{-1} obtained for the activation energy E_a of the corrosion process in 1.0 M HCl lies in the range of the most frequently cited values, the majority of which are grouped around 60 kJ mol^{-1}[23].

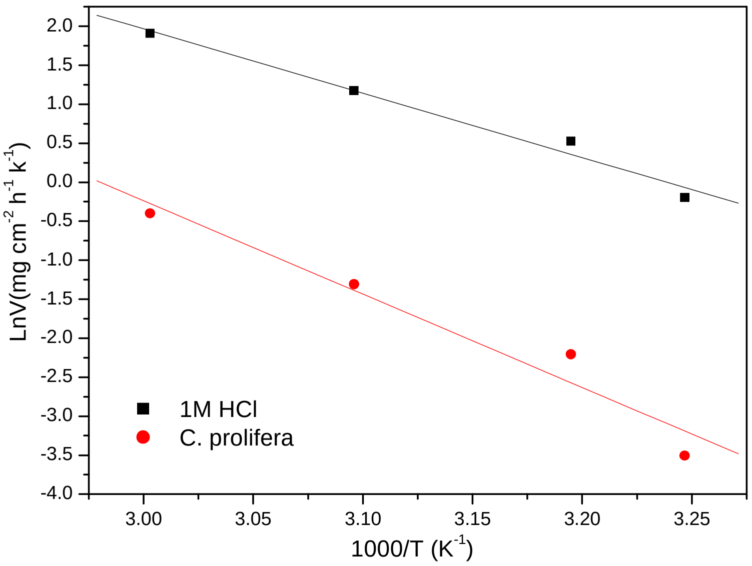

Figure 2. Arrhenius plots of LnVvs. 1/T for mild steel in 1.0 M HCl in the absence and the presence of C. proliferaat optimum concentration

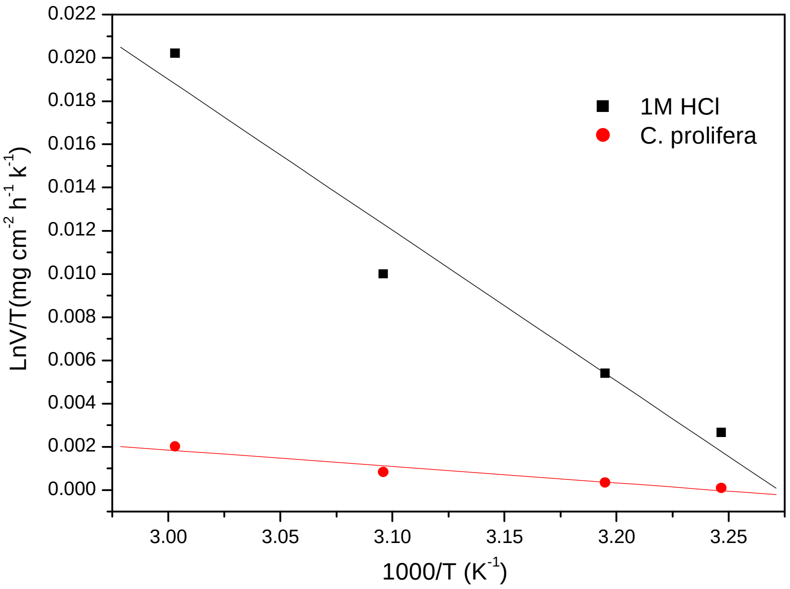

Figure 3. Arrhenius plots of Ln(CR/T) vs. 1/T for steel in 1M HCl in the absence and the presence of C. prolifera at optimum concentration

Table 2.Activation parameters for the steel dissolution in 1.0 M HCl in the absence and the presence of C. prolifera extract at optimum concentration

Inhibitor	A (mg/cm^2 h)	Lin.reg.coef (r)	Ea (kJ/mol)	ΔHa (KJ/mol)
1M HCL	3.92534E+11	0.99057	63.50	57.97
C. prolifera	3.03501E+15	0.97564	99.40	6.33

Inspection of Table 2 showed that the value of Ea determined in 1M HCl containing compound is higher (99.40kJ mol^{-1}) than that for uninhibited solution (63.50kJ mol^{-1}). The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage [24].The positive sign of ΔH_areflect the endothermic nature of the steel dissolution process suggesting that the dissolution of steel is slow [25] in the presence of inhibitor.

3.1.2. Adsorption isotherm

In order to gain more information about the mode of adsorption of C. prolifera on the surface of mild steel, the experimental data have been tested with several adsorption isotherms, including Langmuir, Frumkin, Freundlich and Temkin isotherms. However, the best fit was obtained from the Langmuir isotherm. Correlation between surface coverage (θ) defined by E_w% / 100 and the concentration of inhibitor (C) can be represented by the Langmuir adsorption isotherm, the isotherm is given by [26]:

$$\frac{C_{\mathrm{inh}}}{\theta} = \frac{1}{K_{\mathrm{ads}}} + C_{\mathrm{inh}} \tag{8}$$

Where K_{ads} is the adsorption constant, C_{inh} is the concentration of the inhibitor and surface coverage values (θ) are obtained from the weight loss measurements for various concentrations. K_{ads} is the equilibrium constant of the adsorption process and is related to the standard Gibbs energy of adsorption,ΔG_{ads} , according to [27]:

$$K_{\mathrm{ads}} = \frac{1}{55.55}\exp\left(\frac{-\Delta G^{\mathrm{o}}_{\mathrm{ads}}}{RT}\right) \tag{9}$$

Where *R* is the universal gas constant and *T* is the absolute temperature. The value 55.5 in the above equation is the concentration of water in solution in mol/L. Thermodynamic parameters are important to study the inhibitive mechanism. The values of K_{ads}, R^2 and ΔG_{ads} are calculated and are (out) given in Table 3. The relation between C_{inh}/θ and C_{inh} is shown in Fig. 4. These plots are linear with a slope equal to unity. This suggests that the adsorption of C. prolifera extract on metal surface followed the Langmuir adsorption isotherm. This isotherm assumes that the adsorbed molecule occupy only one site and there are no interactions with other adsorbed species [28-30].

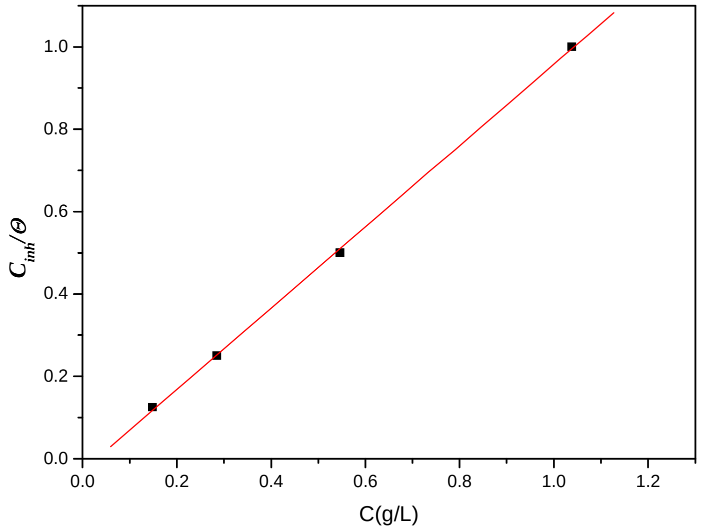

Figure 4. Langmuir adsorption of C. proliferaon the mild steel surface in HCl solution

The correlation coefficient, R^2, was used to choose the isotherm that best fits the experimental data. The strong correlation ($R^2 > 0.999$) suggests that the adsorption of inhibitor on the carbon steel surface obeyed this isotherm.

Table 3. Thermodynamic parameters for the adsorption of C. prolifera in 1.0 M HCl on the mild steel at 308K

Inhibitor	Slope	K_{ads} (M^{-1})	R^2
C. prolifera	0.98651	34.56	0.999

3.2. Potentiodynamic polarization curves:

Potentiodynamic polarization curves of carbon steel in 1.0 M HCl containing C. prolifera at 308K are shown in Fig. 5. The electrochemical corrosion parameters including corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodicTafel slope (βc) and inhibition efficiency (E_P(%)) values were derived from cathodic current–potential curves are presented in Table 4. The E_P(%) was calculated from polarization measurements according to the relation given below [31]:

$$E_p(\%) = \frac{I_{\mathrm{corr}} - I_{\mathrm{corr(i)}}}{I_{\mathrm{corr}}} \times 100 \tag{10}$$

where I_{corr} and $I_{\mathrm{corr(i)}}$ are the corrosion current densities for steel electrode in the uninhibited and inhibited solutions, respectively.

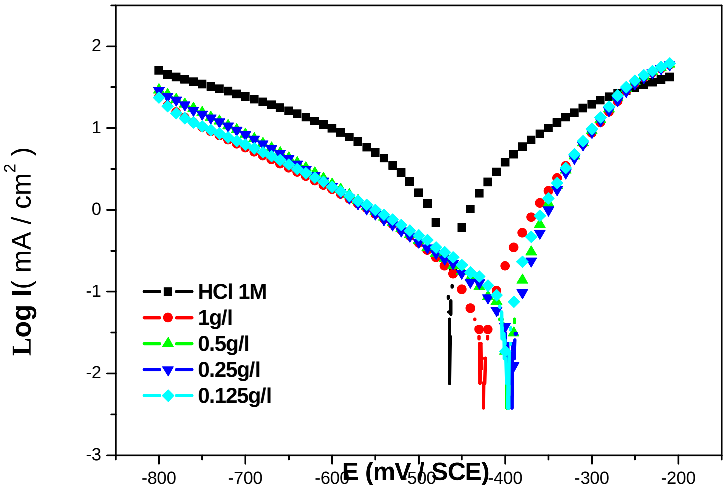

Figure 5: Tafel plot of mild steel with different concentrations of C. prolifera in 1M HCl solution

Inspection of the figure 5 shows that the addition of C. prolifera has an inhibitive effect in the both anodic and cathodic parts of the polarization curves and generally shifted the E_{corr} value towards the positive direction compared to the uninhibited mild steel. Thus, addition of this inhibitor reduces the mild steel dissolution as well as retards the hydrogen evolution reaction. The presence of C. prolifera does not prominently shift the corrosion potential, which indicates the studied C. prolifera inhibitor act as mixed-type inhibitor [32, 33]. Furthermore, in the presence of this inhibitor, the slight change of βc indicates that the cathodic corrosion mechanism of steel does not change.

Table 4: Tafel polarization parameters obtained at different concentrations of C. prolifera

Inhibitors	Concentration (g/l)	$-E_{\mathrm{corr}}$(mV/SCE)	I_{corr} (µA/cm^2)	-βc	E_p (%)
1M HCl	-	464	1386	164	--
C. prolifera	**1**	397	70	134	94.95
	0.5	394	72	143	94.81
	0.25	398	97	147	93.00
	0.125	425	162	147	88.31

3.2. Electrochemical impedance spectroscopy

The corrosion behaviour of mild steel, in acidic solution in the presence and absence of inhibitor, is investigated by the electrochemical impedance spectroscopy (EIS) at 308 K after 30 min of immersion. Fig. 6 show the EIS diagrams carried out at 208 K in acid solution with and without C. prolifera. The impedance parameters derived from these investigations are mentioned in Table 5.

$$E\% = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} * 100 \tag{11}$$

Where $Rct_{(inh)}$ and R_{ct} are the charge transfer resistance in the presence and absence of C. prolifera.

The charge transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [34]. The double layer capacitance (C_{dl}) and the frequency (f_{max}) at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation:

$$C_{dl} = \frac{1}{(w.R_{ct})} \quad \text{with} \quad \omega=2\pi f_{\max} \qquad (12)$$

where C_{dl}: Double layer capacitance ($\mu F.cm^{-2}$); $f_{\max}$: maximum frequency (Hz) and R_{ct}: Charge transfer resistance ($\Omega.cm^2$)

It is also clear that these impedance diagrams consist of one large capacitive loop and they are not perfect semicircles and this difference has been attributed to frequency dispersion [35, 36] and the heterogeneity of the metal surface [37- 39].

In order to fit and analyze the EIS data, an equivalent circuit was selected and is shown in Fig. 7. This circuit is generally used to describe the mild steel/acid interface model [40, 41]. Excellent fit with this model was obtained with our experimental data. As an example, the Nyquist and Bode plot for C. prolifera at 1g/L in 1M HCl are presented in fig. 8a and 8b, respectively. The values of inhibition efficiency were calculated using the relation:

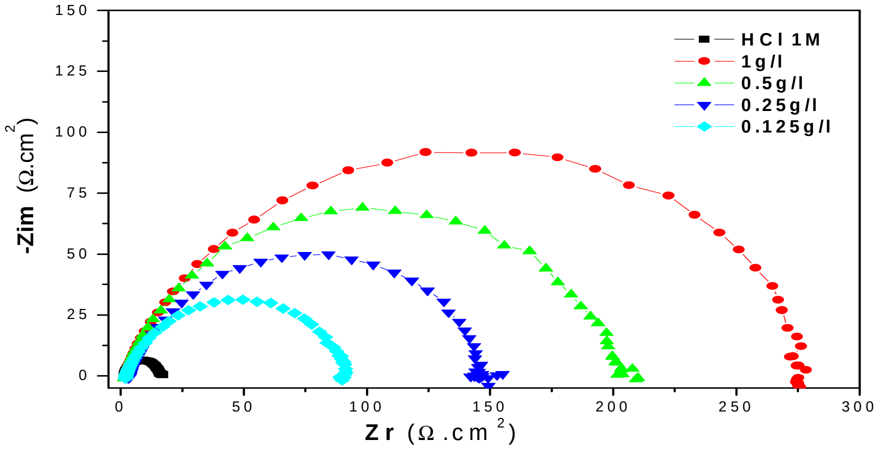

Figure 6: Nyquist plot at different concentrations of C. prolifera in 1M HCl solution

Table 5: Impedance parameters for mild steel in 1M HCl in the absence and presence of different concentrations of C. prolifera

Inhibitor	Concentration (g/l)	R_{ct} ($\Omega.cm^2$)	R_b ($\Omega.cm^2$)	C_{dl} ($\mu f/cm^2$)	E (%)
1M HCl	-	14.57	1.37	200	--
C. prolifera	**1**	276	1.51	46.09	94.72
	0.5	202	1.52	49.78	92.79
	0.25	143	2.86	55.60	89.81
	0.125	91	1.91	70.34	83.99

From table 4, it is clear that the R_{ct} values increase with inhibitor concentration and consequently the inhibition efficiency increases to 94.72 % at 1g/L. In fact, the presence of C. prolifera is accompanied by the increase of the value of R_{ct} in acidic solution confirming a charge-transfer process mainly controlling the corrosion of C-steel. Values of double-layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in the values of C_{dl}. The decrease in C_{dl} is due to the adsorption of the inhibitor on the metal surface leading to the formation of film or complex from acidic solution [42].

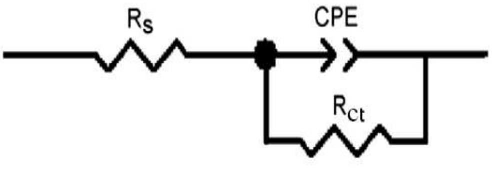

Figure 7. Electrochemical equivalent circuit used for impedance spectra of C. prolifera

In this equivalent circuit, R_S is the solution resistance, R_{ct} is the charge transfer resistance and CPE is a constant phase element. The impedance function of the CPE is as follows:

$$Z_{CPE} = Y^{-1} (j\omega)^{-n} \qquad (13)$$

Where Y is the magnitude of CPE, x is the angular frequency (2pfmax), and the deviation parameter n is a valuable criterion of the nature of the metal surface and reflects microscopic fluctuations of the surface. For n = 0, Z_{CPE} represents a resistance with $R = Y^{-1}$; n = -1 an inductance with $L = Y^{-1}$, n = 1 an ideal capacitor with C = Y [43].

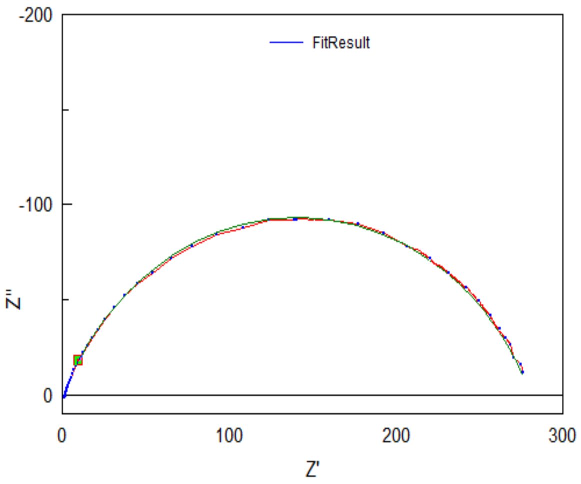

Figure 8a: EIS Nyquist plot for mild steel /1M HCl+1g/L C. prolifera interface: -----experimental (data -----calculated)

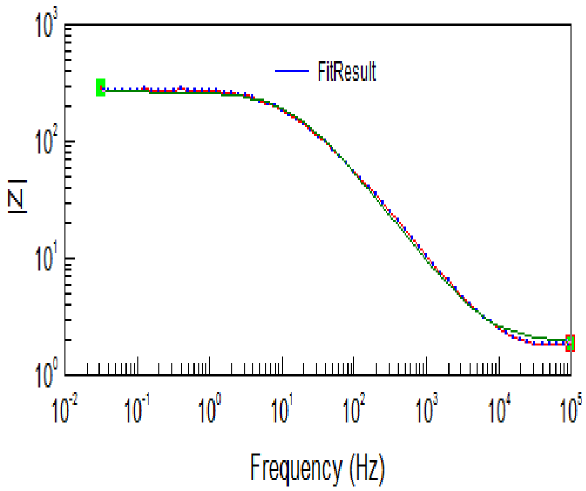

Figure 8b: EIS Bode plot for mild steel /1M HCl+1g/L C. prolifera interface: -----experimental (data -------calculated)

The measured and simulated data fit very well. It is observed that the fitted data follow almost the same pattern as the original results along the whole diagrams, with an average error about 1% in all cases. A quick examination of the electrochemical and EIS parameters indicates that the values of the corrosion potential, anodic and cathodicTafel slopes vary slightly in the presence of C. prolifera concentration. These results suggest that the action of molecules of C. prolifera act by pure geometric blocking of the electrode surface.

CONCLUSION

The results revealed the inhibitive effect of C. prolifera which acted as mixed type inhibitor. The inhibition efficiency was found to increase with increasing concentration of the algal extract but decreased with increase in temperature which is attributed to the physisorption. The results ob tained from the polarization technique were in good agreement with those obtained from the electrochemical impedance spectroscopy (EIS) and gravimetric method with a small variation. The inhibition action of the studied compound is mainly due to their adsorption on the mild steel surface. Adsorption process obey Langmuir adsorption isotherm. The thermodynamic parameters (K_{ads},ΔG_{ads}) of adsorption for the studied compounds are calculated from their adsorption isotherms. The negative values of ΔG_{ads} show the spontaneity of the adsorption. The impedance measurements at the corrosion potential showed a single capacitive looprelated to dielectric properties of the surface film.

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