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Carbon Steel Corrosion Inhibition by Rind and Leaves Extracts of Grapefruit in 1.0 M Hydrochloric Acid

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Abstract

Extract of grapefruit rind (GFR) and grapefruit leaves (GFL) was investigated as corrosion eco-friendly inhibitor of carbon steel in 1.0 M HCl acid using a conventional weight loss measurements, electrochemical technique as potentiodynamic polarization methods and electrochemical impedance spectroscopy (EIS) techniques. The electrochemical polarization data revealed the mixed mode of inhibition. The obtained results showed that all the extracts are excellent corrosion inhibitors and their adsorption on the carbon steel surface follows the Langmuir isotherm model in acidic media. The results of electrochemical impedance spectroscopy have shown that the change in the impedance parameters, charge transfer resistance and double layer capacitance, with the change in concentration of the extract is due to the adsorption of active molecules leading to the formation of a protective layer on the surface of carbon steel. The extracts were found to inhibit the corrosion of carbon steel in 1.0 M HCl solutions and the inhibition efficiencies of the extracts follow the trend: GFR>GFL. Some thermodynamic functions of dissolution process were also determined and discussed.

1. Introduction

The economic importance of carbon steel has increased due to its great demand in various industries; however its tendency to corrosion. Acid solutions are used in industry to remove mill scale from metallic surfaces [1-2]. Hydrochloric acid is often used because of the higher soluble ferrous chloride. One way of protecting steel from corrosion is to use corrosion inhibitors. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty [3]. Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available renewable sources of materials and ecologically acceptable. Plant products are organic in nature, and some of the constituents including tanins, organic and amino acids, alkaloids, and pigments are known to exhibit inhibiting action [4]. Moreover, they can be extracted by simple procedures with low cost and they are green inhibitors. By definition, green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment [5]. Many authors have been investigated a variety of natural products [4,6–10] and several plants and their different body parts as corrosion inhibitors [11-36].

Grapefruits are low in calories but are full of nutrients and an excellent source of vitamins A and C. Harvard Medical School states that grapefruit has a glycemic index of 25, suggesting that it does not significantly affect blood sugar and insulin levels [37]. You can find out more about the nutritional breakdown of grapefruits in the nutritional profile section of this article. [38]Choosing to regularly eat lycopene-rich foods, such as pink grapefruit, and drink green tea may greatly reduce a man's [39] risk of developing prostate cancer, suggests research published the Asia Pacific Journal of Clinical Nutrition.

This work is to investigate the corrosion inhibition of grapefruit extract GFR and GFL in 1.0 M HCl solutions using polarization curves, impedance spectroscopy (EIS) and weight loss measurements. Effects of inhibitor concentration, temperature on the corrosion inhibition were fully investigated and discussed.

2. Materials and methods

2.1. Materials and Solutions

The steel that we used in this study is a carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) 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 remainder iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (320, 800 and 1200); rinsed with distilled water, degreased in acetone, washed again with bidistilled water and then dried at room temperature before each use. The 1.0 M HCl solution was prepared by dilution of an analytical reagent grade 37% HCl with double-distilled water. Grapefruit rind (GFR) and grapefruit leaves (GFL) were collected from the area of Taroudant (located in Morocco). Leaves and rind plant were dried and crushed. Stock solution of the extract was prepared by stirring cold weighed amounts of the GFR and GFL plant for 48 h in 1.0 M HCl solution. The resulting solution was filtered and the tested mediums are prepared by dilution. This extract was used to study the corrosion inhibition properties~~.~~ The solution tests are freshly prepared before each experiment. The concentration range of the inhibitor employed was 0.05 g/L to 0.5 g/L.

2.2. Weight loss measurements

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume was 100 ml. The steel specimens used had a rectangular form (2 x 2 x 0.08 cm^3) immersed in acid solution 1M HCl for 6 hours. All solutions were prepared with bidistilled water. The experiments were performed in aerated solutions at 298K using a thermostatic bath.

2.3. Polarization measurements

2.3.1. Electrochemical impedance spectroscopy (EIS)

The electrochemical measurements were carried out using Voltalab (PGZ 100) potentiostate and controlled by software model (Voltamaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE), all potentials given in this study were referred to this reference electrode. A platinum electrode was used as auxiliary electrode. The working electrode was carbon steel. The working electrode was immersed in test solution for 30 minutes to a establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp}, the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 298 K. The system impedance is measured as a function of the frequency of the applied signal between 1 mHz and 100 kHz and its value is given in the complex plane for each frequency. The resulting Nyquist plot comprises one semi-circle whose distance to the origin indicates the resistance of the electrolyte and the amplitude indicates the transfer resistance of the electrode.

2.3.2. Polarization curves

The electrochemical study is one of the most commonly used techniques to determine a corrosion rate. Indeed, its experimental tests appear to be extremely simple and fast. The method has been used to speed up certain types of corrosion or deterioration. But its main use is for plotting polarization curves. In addition, the program allows Voltamaster 4 trace the current logarithmic scale and the use of Tafel method allows us to determine the value of corrosion current and other electrochemical parameters. The current-potential curves were obtained by potentiokinetic mode in the 1.0M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -800 mV to -200 mV versus corrosion potential with a potential scan rate of 1 mV/s. This value is sufficiently low, which allows to approach as much as possible the conditions of the steady state of the system studied.

3. Results and discussion

3.1 Polarization results

The characteristics of current–potential curves resulting from cathodic and anodic polarization of steel in 1.0M HCl with various concentrations of GFR and GFL extract have been evaluated. Fig. 1 shows the potentiodynamic polarization curves containing various concentrations of GFR and GFL extract at 298 K. The corrosion parameters including corrosion potential (E_{corr}), current densities (I_{corr}), cathodic Tafel slope (β_c), and inhibition efficiency (E_I %) are listed in Table 1. The inhibition efficiency is calculated following the relationship:

$$E_I\,(\%) = \left(1 - \frac{I'_{corr}}{I_{corr}}\right) \times 100 \qquad (1)$$

Here, I_{corr} and I'_{corr} are current density in the absence and presence of the studied extracts respectively. We noted that I_{corr} and I'_{corr} were determined by extrapolation of cathodic Tafel lines to the corrosion potential.

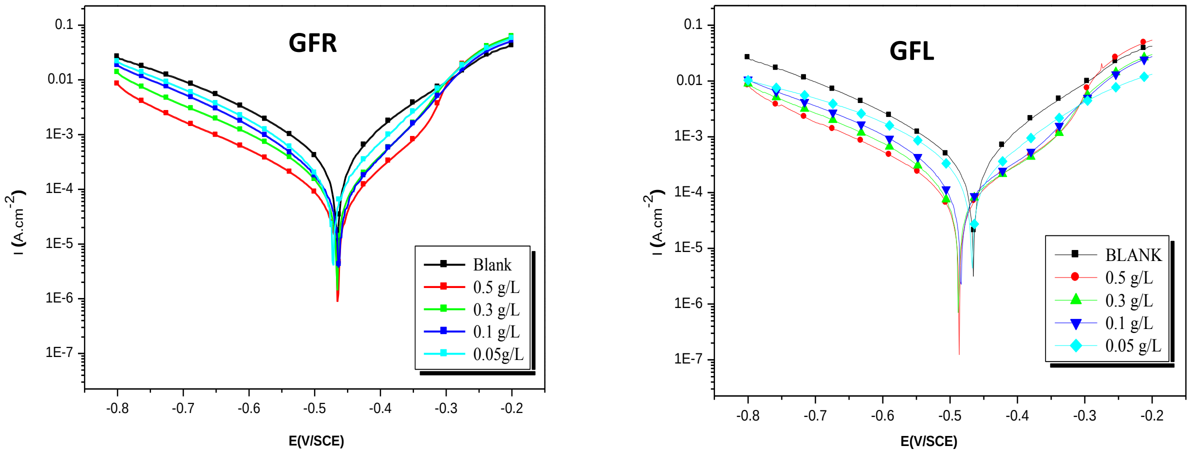

Figure 1: Potentiodynamic polarization curves for carbon steel immersed in 1.0 M HCl solution in the absence and presence of various concentrations of GFR and GFL extract.

Table 1: Data obtained from potentiodynamic polarization measurements of carbon steel immersed in 1.0 M HCl solution in the absence and presence of various concentrations of the tow extracts.

Inhibitor	**Concentration (g/L)**	**$-E_{corr}$ (mV/SCE)**	**I_{corr}(µA/cm^2)**	**$-\beta_c$ (mV/dec)**	**E_I (%)**
Blank	0	463	636	168	-
GFR	0.5	464	82	173	87.10
	0.3	467	171	178	73.11
	0.1	460	228	175	64.15
	0.05	471	331	172	56.80
GFL	0.5	486	132	173	79.24
	0.3	488	235	195	63.05
	0.1	483	294	213	53.77
	0.05	467	342	286	46.23

From electrochemical polarization measurements, it is clear from the results shown in Table .1 that the addition of inhibitor causes a decrease of the current density. This decrease can be explained by the inhibitory action of these inhibitors. The parallel cathodic Tafel plots obtained in Fig. 1 indicate that the hydrogen evolution is activation-controlled and the slight change of both βc indicates that this reduction mechanism is not affected by the presence of inhibitor. In the anodic domain (Fig. 1), the polarization curves of carbon steel have shown that the addition of the inhibitors decreases the current density acting mainly on the dissolution reaction of metal. The addition of GFR extract show that a desorption process appears at high potential (Fig.1) [36]. The polarization curves for carbon steel in 1.0 M HCl show that the presence of the both grapefruit extracts inhibits both cathodic and anodic process. This phenomenon is more pronounced with the concentration of inhibitors. The inhibition efficiency (E_I%) increases with inhibitor concentration reaching 87.10% for GFR extract and 79.24 % for GFL at 0.5 g/L. These results suggest that these inhibitors acts as a good corrosion inhibitor mixed character.

3.2. Electrochemical impedance spectroscopy measurements (EIS)

EIS technique was applied to investigate the electrode /electrolyte interface and corrosion processes that occur on carbon steel surface in the absence and presence of GFR and GFL extracts. EIS measurements were made at open circuit potential in a wide frequency range at 298K, to confirm complete characterization of the interface and surface processes. Fig.2 show Nyquist plots for carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of GFR and GFL extract at the open circuit potential. The values of the charge-transfer resistance (R_t) were obtained from the difference in real component of impedance at lower and higher frequencies as suggested by Tsuru and Haruyama [37]. The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation [38]:

$$c_{dl} = (2\pi . f_{\max} . R_{t)})^{-1} \qquad (2)$$

Where f_{max} is the frequency value at which the imaginary component (Z_{im}) of impedance is maximum. The inhibition efficiency can be calculated by the following formula:

$$E_{RT}\,(\%) = \;(1 - \frac{R_t^0}{R_t}) \times 100 \qquad (3)$$

Were R_t and $R°_t$ are the charge transfer resistances in inhibited and uninhibited solutions respectively. The data obtained from fitted spectra are listed in Table .2.

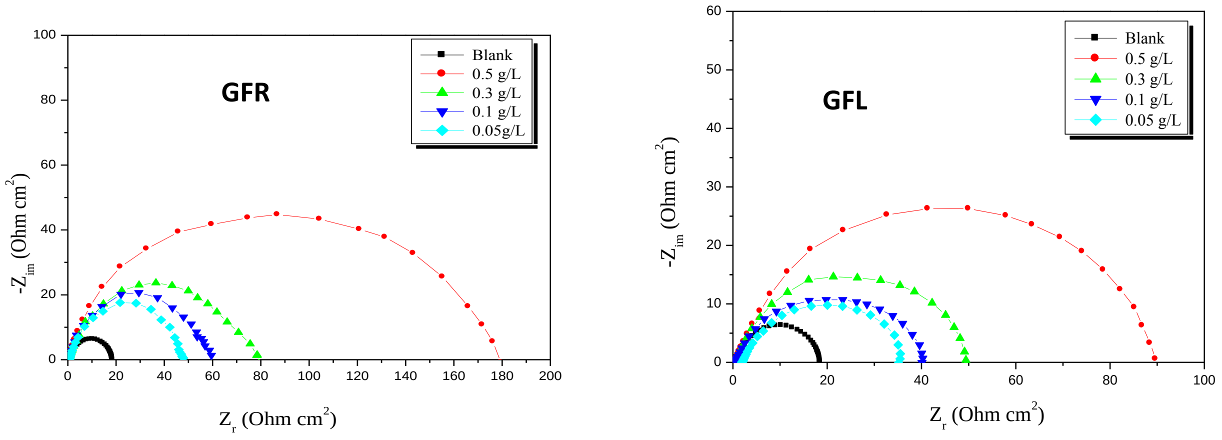

Figure 2: Nyquist plots for carbon steel immersed in 1.0M HCl solution in the absence and presence at various concentrations of GFR and GFL extract at E_{corr} after 30 min of immersion.

The Nyquist plots are significantly changed on addition of the inhibitors, and the impedance of the inhibited system increased with inhibitor concentration. The obtained Nyquist impedance diagrams consists of one large capacitive loop in both cases does not show perfect semicircles, generally attributed to the frequency dispersion [42, 43] as a result of roughness and heterogeneity of the metal surface [44, 45]. The diameter of the semicircle increases with the increase in extracts concentration in the electrolyte, indicating an increase in corrosion resistance of the material [46]. The most marked effect and highest charge-transfer resistance R_t is for GFR extract.

The Bode plot, Fig.3 shows resistive region at high frequencies and capacitive region at intermediate frequencies but do not show a clear resistive region at low frequencies. These plots show two overlapped phase maxima at intermediate and low frequencies. According to act circuit theory, an impedance plot obtained for a given electrochemical system can be correlated to one or more equivalent circuits. The obtained results for carbon steel electrode in acidic solutions in the presence of different extracts concentrations were characterized by one capacitive loop and analyzed using the equivalent circuit shown in Fig.4 were presented the charge transfer resistance (**R_t**) in parallel to the capacitance (**C_{dl}**) connected with the electrolyte resistance (**R_e**). From these Nyquist plots, the difference in real impedance at lower and higher frequencies is generally considered as charge-transfer resistance.. The adsorption of extracts molecules on the metal surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the metal surface. This modification results in an increase of charge-transfer resistance. Data collected are gathered in Table 2.

Data given in Table 2 indicate that the R_t values increased with inhibitors concentrations and consequently the inhibition efficiency increases. The maximum E_{RT}(%) values are 90%, and 80 % for GFR and GFL respectively, may suggest the formation of a protective layer on the carbon steel surface. This layer makes a barrier for mass and charge-transfer. By increasing the extracts concentrations, the calculated C_{dl} values decrease, as it can be seen from Table. 2 the C_{dl} values tend to decrease with the increase of the concentration of Grape fruit extract. In 1.0 M HCl solution. The decrease in the C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the extracts molecules function by adsorption at the metal/solution interface [47]. The inhibition efficiencies E_{Rt}(%) calculated from impedance data are very close to those obtained from potentiodynamic polarization measurements. The order of inhibition efficiency obtained from EIS measurements is as follows:

GFR > GFL

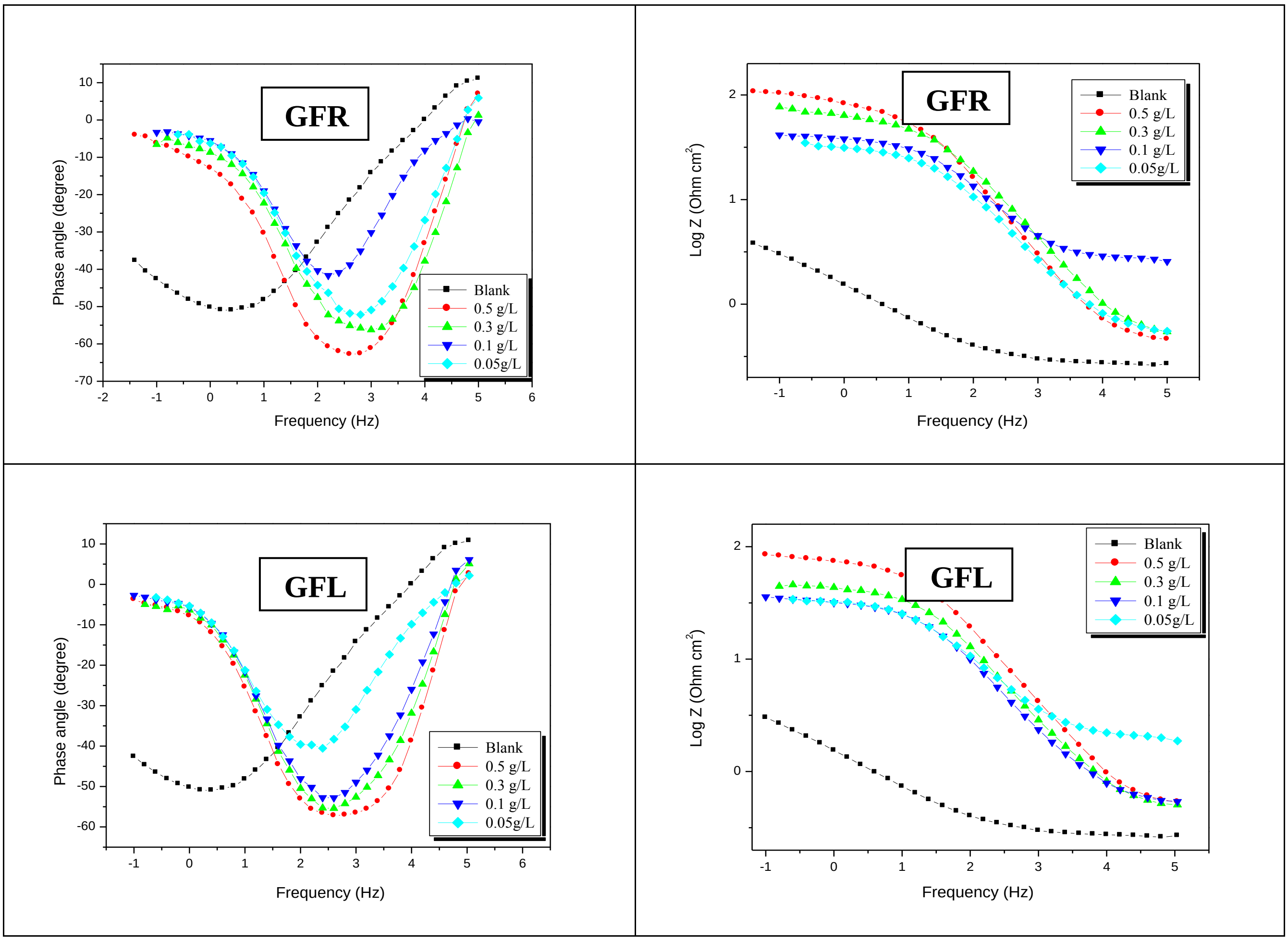

Figure 3: Bode plots for carbon steel in 1 M HClat different concentrations of GFR and GFL extracts

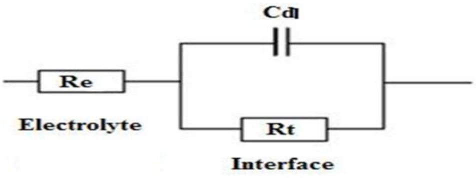

Figure 4: Equivalent circuit proposed to fit the EIS experimental data

Table 2: Data from electrochemical impedance spectroscopy measurements of carbon steel in 1.0 M HCl solution in the absence and presence of various concentrations of the inhibitors.

Inhibitor	**Concentration (g/L)**	**R_t (Ω.cm^2)**	**C_{dl} (μF.cm^{-2})**	**E_{RT} (%)**
1.0 M HCl	0.0	18	221.16	-
GFR	0.5	180	35.38	90.00
	0.3	80	49.76	77.50
	0.1	60	176.92	70.00
	0.05	47	225.52	61.70
GFL	0.5	90	117.95	80.00
	0.3	50	127.39	64.00
	0.1	40	159.24	55.00
	0.05	35	181.98	48.57

3.3. Weight loss measurements

The chemical measurements were carried out by weight loss methods as previously described [38]. This method of monitoring corrosion rate and inhibition efficiency is useful because of its simple application and high reliability [48]. Fig. 5 shows the corrosion rate W_{corr} values of carbon steel with and without different concentrations of GFR and GFL extract in 1.0 M HCl.

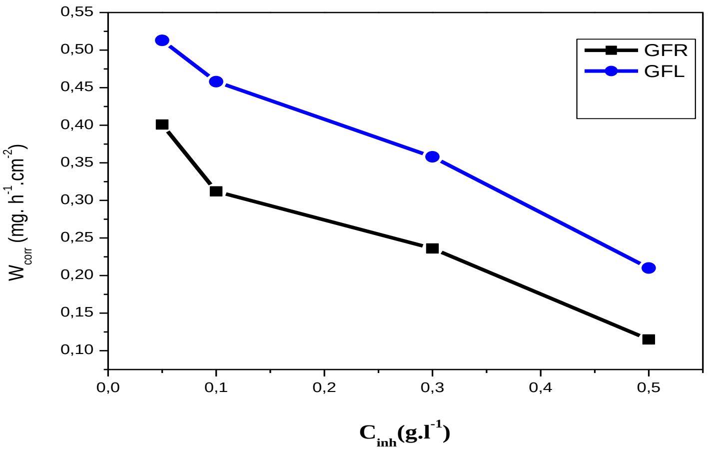

Figure 5: Relationship between corrosion rate (W) and concentration of inhibitor (C) in 1.0M HCl at 298K

The corrosion rates (W_{corr}) and the inhibition efficiencies Ew(%) for carbon steel in absence and presence of different concentrations of GFR and GFL extract at 298K are given in Tables 3

Table 3: Corrosion parameters obtained from weight loss measurements for carbon steel in 1.0M HCl containing various concentrations of GFR and GFL extractsat 298 K.

Inhibitor	**Concentration (g/L)**	**W_{corr}(mg. h^{-1}.cm^{-2})**	**E_w (%)**
Blank	0.0	1.002	-
GFR	0.5	0.115	88.52
	0.3	0.236	81.83
	0.1	0.312	68.86
	0.05	0.401	59.98
GFL	0.5	0.21	79.14
	0.3	0.358	64.27
	0.1	0.458	54.29
	0.05	0.513	48.80

In the case of the weight loss method, the inhibition efficiency (Ew %) was determined by the following equation:

$$E_W(\%) = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \qquad (4)$$

Where W_{corr} and W'_{corr} are the corrosion rate of carbon steel in 1.0 M HCl in absence and presence of inhibitor, respectively.

Analysis of the results of Table 3 and Fig.4, we clearly shows that the GFR and GFL extracts at 298 K inhibitory possesses interesting inhibiting properties of corrosion of carbon steel in 1.0 M HCL medium studied as mentioned by Cristofari [49]. The variation of the inhibition efficiency of the extracts studied according to the results given in (Table 3). It appears that the corrosion rate decreases, which lead to an increase of the effectiveness of the protection with the inhibitor concentration, which reaches a maximum value of 88.52% for GFR and 79.14% for GFL extract at 298K at a concentration of 0.5 g / L. This decrease in corrosion rate is likely due to the adsorption of molecules of the inhibitor on the surfacemetal and forming a molecular film layer or barrier between the metal and the corrosive medium according to Obot [50]. It is clear that the inhibitory action for GFR is widely remarked when compared to GFL extract. The results obtained from weight loss method are a good agreement with electrochemical studies.

3.4. Adsorption isotherm

The action of an inhibitor in the acid medium is assumed to be due to its adsorption to the metal/solution interface. The kind of adsorption isotherm can give more information about the properties of the studied extracts. Several adsorption isotherms were tested and the Langmuir adsorption isotherm was found to furnish best description of the adsorption behaviour of the studied extracts. The Langmuir isotherm is given by the following equation [51]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (5)$$

Where C_{inh} is the inhibitor concentration, θ the fraction of the surface covered determined by Ew(%)/100, K_{ads} the equilibrium constant. Plots of C_{inh}/θ against C_{inh} yield straight lines as shown in Fig.6.

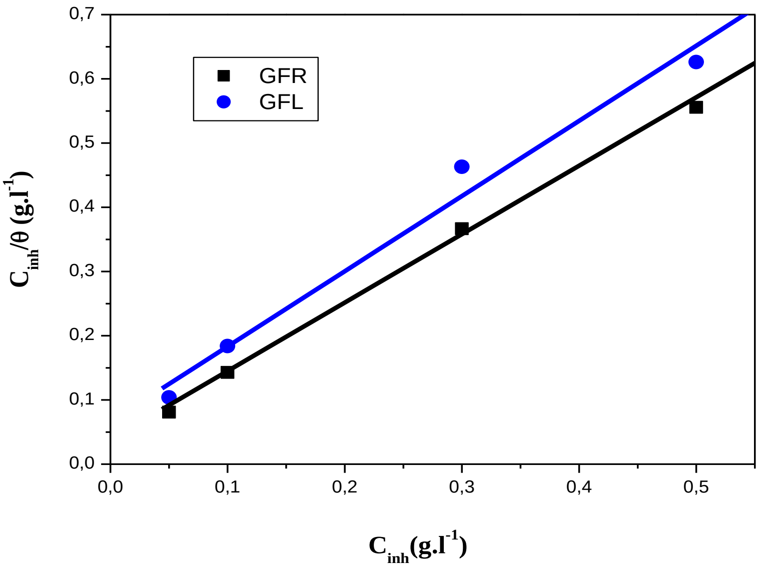

Figure 6: Langmuir adsorption plots for carbon steel in 1.0 M HCl at 298K in the presence different concentration of GFR and GFL extracts.

An excellent fit was obtained for both extracts grapefruit plant, using the following Langmuir adsorption isotherm. Straight line plots were obtained with the slope and linear correlation coefficient R are close to 1. These results show that the adsorption of both extracts grapefruit plant obeyed to the Langmuir isotherm. Examination of literature shows that extract contains various components revealed the presence of flavonoids [52,53], ascorbic acid, tocopherols, citric acid [54], limonoids [55,56],specially methyl-p-hydroxybenzoate and 2,4,4'-trichloro-2'-hydroxydiphenylether (triclosan) [57]. The infinite compounds let to assume that the inhibition process is essentially due to the synergistic intermolecular phenomenon between molecules of natural product [58-60].

Effect of temperature

The effect of temperature on the corrosion rate of steel in 1.0 M HCl with the addition of the tow extracts inhibitors is made from 298 to 328 K as shown in Table 4 using electrochemical impedance spectroscopy measurements technique. The values of R_t decrease with increasing temperature both in uninhibited and inhibited solutions and the efficiency of inhibition by GFR and GFL extracts decreases slightly with increasing temperature. The results confirm that both by GFR and GFL extracts acts as an efficient inhibitor in the range of temperature studied.

On the other hand, the values of R_t were employed to calculate values of the corrosion current density (I_{corr}) at various temperatures in the absence and presence of both GFR and GFL extracts using the following equation [61]:

$$I_{corr} = R.T.(z.F.R_t)^{-1} \qquad (6)$$

where R is the universal gas constant (R = 8.31 J $K^{-1}mol^{-1}$), T is the absolute temperature, z is the valence of iron (z = 2), F is the Faraday constant (F = 96485 coulomb) and R_t is the charge transfer resistance.
The logarithm of the corrosion rate of carbon steel I_{corr} can be represented as a straight-line function of 1000/T (Arrhenius equation, Fig.7)

$$I_{corr} = A\exp\left(-\frac{E_a}{R.T}\right) \qquad (7)$$

where A is Arrhenius factor, Ea is the apparent activation corrosion energy, R is the perfect gas constant and T the absolute temperature.

Table 4: Effect of temperature on the carbon steel corrosion in free acid and at 0.5g/L of different inhibitors.

Inhibitor	**Temperature (K)**	**R_t ($\Omega.cm^2$)**	**C_{dl} ($\mu F/cm^2$)**	**E_{RT}(%)**
Blank	298	18	221	-
	308	11	230	-
	318	8	199	-
	328	5	202	-
GFR	298	180	35	90.00
	308	62	103.73	82.26
	318	45	141.54	82.22
	328	34	74.34	85.30
GFL	298	90	117.95	80.00
	308	45	235.90	75,55
	318	35	454.96	77,14
	328	20	530.79	75.00

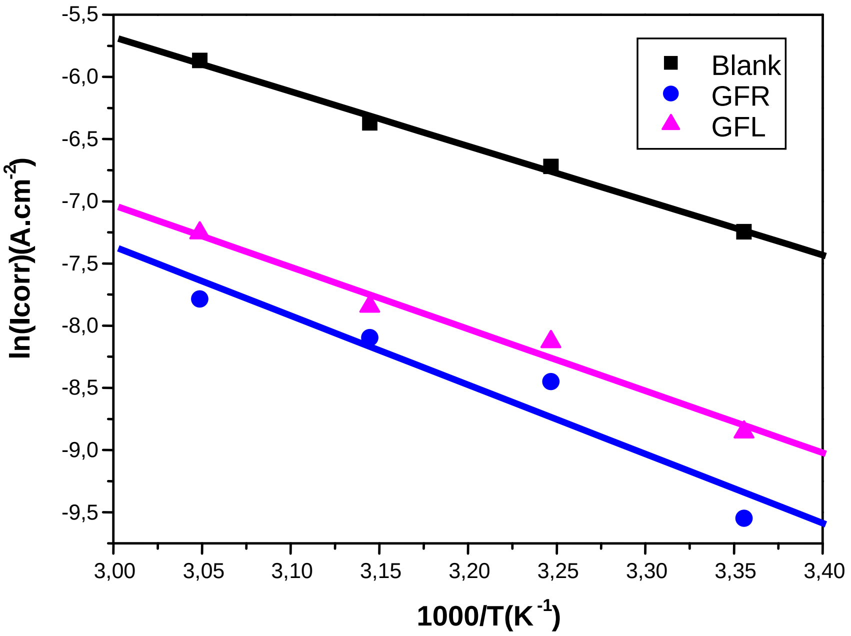

Figure 7: Arrhenius plots of carbon steel in 1.0 M HCl with and without 0.5 g/L of the two extracts.

The value of E_a can be calculated from the slope of the straight line of Arrhenius plots. The higher value of Ea in the presence of both GFR and GFL extracts than its absence indicates a strong inhibitive action of the extracts by increasing the energy barrier for the corrosion process [62]. And the higher Ea value in the inhibited solution can be attributed to process of electrostatic adsorption of the tested compounds on the carbon steel surface [63] and the increased thickness of the double layer.

However, the adsorption phenomenon has been successfully explained by thermodynamic parameter, to further elucidate the inhibition properties of inhibitors, the kinetic model was another useful tool to explain the mechanism of corrosion inhibition for the inhibitor. The activation parameters for the corrosion process were calculated from Arrhenius equation:

$$I_{corr} = \frac{R.T}{Nh}.\exp(\frac{\Delta S^*}{R}).\exp(-\frac{\Delta H^*}{RT}) \quad (8)$$

where h is Planck's constant, N Avogadro's number, R the universal gas constant, ΔH* the enthalpy of the activation and ΔS* is the entropy of activation.

Fig. 8 presented the plot of Ln(I/T) against 1000/T. Straight lines were obtained with a slope of (ΔH* /R) and an intercept of (Ln(R/N.h) + (ΔS*/R)) used to calculate the values of ΔH* and ΔS* shown in listed in Table 5.

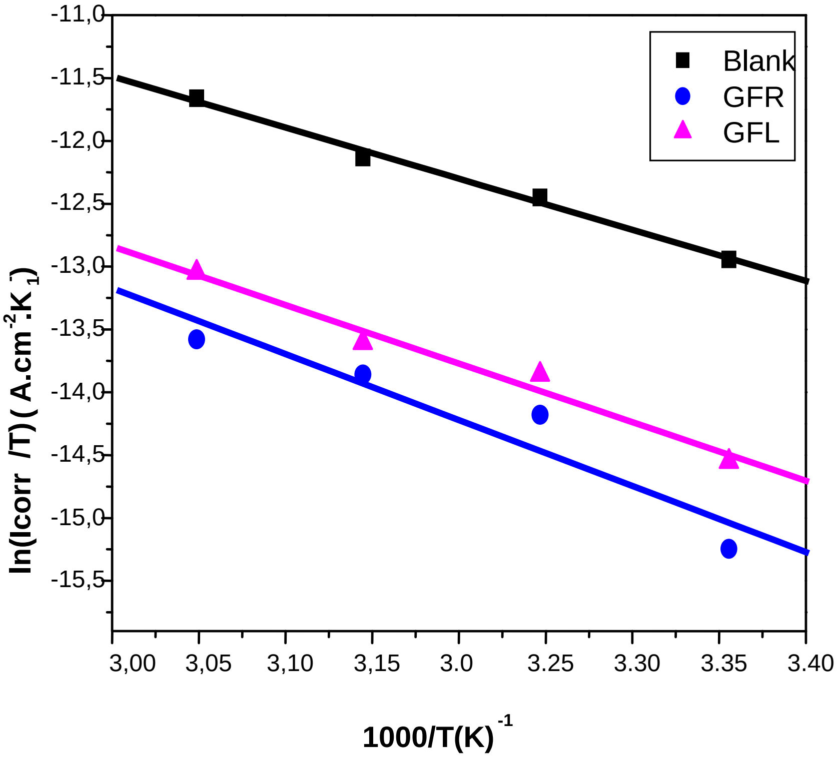

Figure 8: Relation between ln(I/T) and 1000/T in acid at different temperatures in the absence and presence of 0.5 g/L of GFR and GFL extracts.

Table 5: The value of the kinetic parameters for carbon steel in 1.0 M HClin the absence and presence of 0.5 g/L of GFR and GFL extract.

Inhibitor	**ΔH*(kJ/mol)**	**ΔS*(J/mol)**	**Ea (kJ/mol)**	**Ea-ΔH***
1.0 M HCl	33.79	-191.53	36.38	2.60
GFR	43.59	-176.10	46.19	2.60
GFL	38.74	-187.92	41.34	2.60

The positive values of ΔH* mean that the dissolution reaction is an endothermic process and that the dissolution of steel is slow in the presence of GFR and GFL extracts [64]. The analysis of the results presented in Table 5 shows that the values of ΔH* and E_a rise with the inhibitor concentration suggest that the energy barrier of corrosion reaction increases with presence of GFR and GFL extracts. This means that the corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_a in the presence of both inhibitors [65]. From Table 5, it is found that Ea values of the inhibited solutions are higher than in uninhibited solutions. The values of Ea are lower than the threshold value of 80 kJ/mol required for chemical adsorption. This means that the adsorption is physical adsorption [66,67].

Conclusion

The investigated extracts of grapefruit are good inhibitors for the corrosion of carbon steel in 1.0 M HCl solution and their act as mixed type inhibitors. The results obtained from potentiodynamic polarization curves and EIS measurements show that the inhibition properties increase with small differences in their efficiencies values. Double layer capacitances decrease with respect to blank solution when these extracts were added. This fact may explained by adsorption of these inhibitors on the Carbon steel surface. The adsorption of the investigated GFR and GFL extracts on the carbon steel surface in HCl solution follow Langmuir adsorption isotherm. Thermodynamic parameters show that both GFR and GFL extract leads to formation of film protective of carbon steel surface. All the technical used in this study indicate that GFR extract inhibit the corrosion process of carbon steel more than GFL.

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