

Electrochemical and thermodynamic study of the inhibitory efficacy of Methanol extracts of the Rind and Leaves of Grapefruit plant on the corrosion of carbon steel in an acidic medium

A. Batah¹, A. Anejjar¹, M. Belkhaouda^{1,2}, L. Bammou^{1,2}, R. Salghi¹, L. Bazzi², B. Hammouti³, A. chetouani^{3,4}

¹Laboratory of Environmental Engineering and Biotechnology, ENSA, Ibn Zohr University, PO Box 1136, 80000 Agadir, Morocco

²Laboratoire Matériaux et Environnement, Faculté des Sciences d'Agadir, 80000. Morocco

²Laboratoire de Chimie Analytique Appliquée, Matériaux et Environnement (LCAME), Faculté des Sciences, Université Mohammed Premier, BP 4808, M-60 000, Oujda, Morocco

⁴ Centre Régional des Métiers de l'Education et de la Formation de l'Oriental, Oujda, Maroc.

Abstract

The inhibition potentials of methanol extracts of leaves (GFL) and rind (GFR) of Grapefruit plant was investigated by evaluating the corrosion behaviour of carbon steel metal immersed in 1.0 M HCl solution containing various concentrations of the extracts. Electrochemical technical, Gravimetric measurements and adsorption characterization were utilized to evaluate the corrosion inhibition and adsorption properties of the extracts. The results revealed that the studied extracts were efficient inhibitors of corrosion in carbon steel immersed in 1.0 M HCl and that the inhibition efficiency depends on the concentration of the extracts. The activation energies and the negative free energy of adsorption obtained from the adsorption of methanol extracts of leaves and rind of Grapefruit indicate that the methanol extracts were physically adsorbed on the surface of the carbon steel and that the adsorption is endothermic, spontaneous, strong and fit excellently with the assumptions of the Langmuir adsorption isotherm. The activation parameters are determined and discussed.

* Corresponding author:

L.bammou@uiz.ac.ma

Received 10 Mai 2017,

Revised 06 Jun 2017,

Accepted 10 Jun 2017

Keywords: Grapefruit, Rind, Carbon Steel, green inhibitor, Leaves, corrosion inhibition

1. Introduction

Corrosion is the deterioration of metal by attack or chemical reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Corrosion affects most industrial sectors and can cost billions of dollars each year [1], for example in the case of industrial processes metals are exposed to the action of acids, which act as corrosive agents. Prevention would be more practical and achievable than complete elimination. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment, for example, formation of oxides, diffusion of metal cations into the coating matrix, and electrochemical potential.[2,3,4,5] The study of corrosion of steel is a matter of tremendous theoretical and practical concern and as such has received a considerable amount of interest. Hydrochloric acid is one of the most widely used agents in the industrial sector. This acid causes degradation of metals, either by chemical or electrochemical reactions. Several industrial technologies use hydrochloric and sulfuric acids in their engineering processes. There are several methods available to protect metals from corrosion in this environment, such as the use of a protective barrier, galvanizing and cathodic protection use of anti-rust solutions or corrosion inhibitors. In this context, the search for corrosion inhibitors in acidic media to protect metallic surfaces has established the natural products as a rich and promising source. Due to environmental concerns, oils and plant extracts are increasingly seen as a source of green corrosion inhibitors. They are used for the protection of metals in the acid environment; in order to replace the toxic chemicals currently used [6]. The selection of the inhibitors is not only based on their inhibition efficiency but also their environmental impact. Inhibitors are [7]: substances which retard the cathodic processes and / or the anodic processes, that inhibitors function in one or more ways to control corrosion: by adsorption of a thin film onto the surface of a corroding material, by inducing the formation of a thick corrosion product, or by changing the characteristic of the environment resulting in reduced aggressiveness. Inhibitors are generally used in these processes to control the metal dissolution. A perusal of the literature on acid corrosion inhibitors reveals that most organic substances employed as corrosion inhibitors can adsorb on the metal surface through heteroatoms such as nitrogen, oxygen, sulfur and phosphorus, multiple bonds or aromatic rings and block the active sites decreasing the corrosion rate [8]. Naturally occurring substances as inhibitors of acid cleaning process have continued to receive attentions as replacement for synthetic organic inhibitors. The greatly expanded interest on naturally occurring substances is attributed to the fact that, not only that they are readily available, ecologically friendly, and pose no threat to the environment but they are cheap and biodegradable and are renewable source of material [9]. Several researches have been done on the use of the extract of plant as inhibitor for metals against corrosion in different aggressive media. However, not much has been reported on the use of the extract of grapefruit plant as inhibitor against corrosion of carbon steel in hydrochloric acid. Most green corrosion inhibitors are obtained from ethanol extract [10-17], some authors are studied methanol extracts as corrosion inhibitors [18, 19]. Several studies show that the use of plant extracts for the protection of metals it possible to achieve high efficiencies [20-29]. Knowing that these products are increasingly seen as a source of green inhibitors. The use of these inhibitors can be effective in different environments (acid, neutral and basic), which can encourage us to replace the toxic chemicals currently used. The aim of this study was to evaluate the inhibitory effects of methanol rind (GFR) and leaf (GFL) Grapefruit extract as corrosion inhibitors for carbon steel in 1.0M HCl acid solution. Potentiodynamic polarization curves, electrochemical impedance spectroscopy, weight loss measurements and also surface morphology analysis were employed to reach this objective. The effects of inhibitor concentration at different temperatures were studied.

2. Experimental procedure

2.1. Gravimetric measurement

This method is a measure of the average corrosion rate. The equipment used is simple. The study is to measure the weight loss of samples surfaces during the time t of immersion of the sample in the corrosive solution maintained at constant temperature. Steel samples of dimensions $1\text{ cm} \times 1\text{ cm} \times 0.2\text{ cm}$. these samples were immersed in 1.0M HCl, without and with addition of different concentrations of inhibitor extract.

Gravimetric experiments were performed in a double glass cell equipped with a thermostated cooling condenser containing 80 mL non-de-aerated test solution. After immersion, the carbon steel specimens were withdrawn, carefully rinsed with bidistilled water, cleaning ultrasonically in acetone, dried at room temperature, and then weighed. The inhibitory efficiency is determined after 24 hours of immersion, at a temperature of 25°C in atmospheric air. The value of the particular inhibitory effectiveness is the average of three tests under the same conditions for each concentration.

2.2. Electrochemical methods

The electrochemical study was carried out using a Volta lab (PGZ 100) potentiostat and controlled by software model (Voltamaster 4) at under static condition. This potentiostat is connected to a cell, with three electrodes, thermostats with double wall. A platinum electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. The material used for constructing the working electrode was the same used for gravimetric measurements. Potentiodynamic polarization curves were plotted at a polarization 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. The registration of these curves is done in the direction of increasing potential. Before all experiments, the potential was stabilized at free potential during 30 min. The polarization curves are obtained from -200 mV to 200 mV at 298 K. The data in Tafel region have been processed for evaluation corrosion kinetic parameters by plotting the polarization curves. The linear Tafel segments, in a large domain of potential, of the cathodic curves were extrapolated to the corresponding corrosion potentials to obtain the corrosion current values.

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 100 kHz and 1 mHz) and its value is given in the complex plane for each frequency. The resulting Nyquist plot comprises one (or more) semi-circle (s) whose distance to the origin indicates the resistance of the electrolyte and the amplitude indicates the transfer resistance of the electrode. For simple systems, the bias resistor can also be obtained by direct reading on the diagram. Experiments are repeated three times to ensure the reproducibility.

2.3. Optical microscopy (OM)

Immersion corrosion analysis of carbon steel samples in the acidic solutions with and without the optimal concentration of the methanol extracts inhibitors was performed using OM. Immediately after the corrosion tests; the samples were subjected to OM studies to examine the surface morphology. OM *Sys Test* was used for the experiments. The working sample was analyzed at three different locations to ensure reproducibility.

3. Result and discussion

3.1. Weight loss, corrosion rates and inhibition efficiency

Weight loss experiments were done according to the method described previously [46]. Weight loss measurements were performed at 298 K for 6 h by immersing the carbon steel coupons into acid solution (80 mL) without and with various amounts of inhibitor. After the elapsed time, the specimen were taken out, washed, dried and weighed

accurately. The inhibition efficiency ($E_w\%$) and surface coverage (θ) was determined by using following equations, where, W_{corr} and $W_{corr(inh)}$ are the weight loss value in the absence and presence of inhibitor :

$$E_w \% = \frac{W_{corr} - W_{corr(inh)}}{W_{corr}} \times 100$$

$$\theta = \frac{W_{corr} - W_{corr(inh)}}{W_{corr}}$$

Initially carbon steel corroded at higher rate in acid but presence of the extracts inhibitor retarded the corrosion rate and remarkable improvement in inhibition efficiency was achieved (Figure.1). It was observed from Figure.1 that corrosion rate was decreasing with increasing inhibitor concentration whereas inhibition efficiency was increased with increasing amount of inhibitor. From data listed in Table.1 decreased value of weight loss was noticed with increasing concentration of inhibitor due to increased surface coverage which can be accounted for inhibitive action of inhibitor.

Table.1: Corrosion parameters obtained from weight loss measurements for carbon steel in 1.0M HCl containing various concentrations of GFR and GFL methanol extracts at 298 K.

Inhibitor	Concentration (g/L)	W_{corr} (mg .cm ⁻² .h ⁻¹)	E_w (%)	θ
Blank	1.00	1.002	-	-
GFL	1.00	0,197	80,33	0.80
	0,50	0,286	71,46	0.71
	0,30	0,352	64,87	0.65
	0,05	0,432	56,89	0.57
GFR	1.00	0.176	82.44	0.82
	0.50	0.221	77.94	0.78
	0.30	0.261	73.95	0.74
	0.05	0.338	66.27	0.66

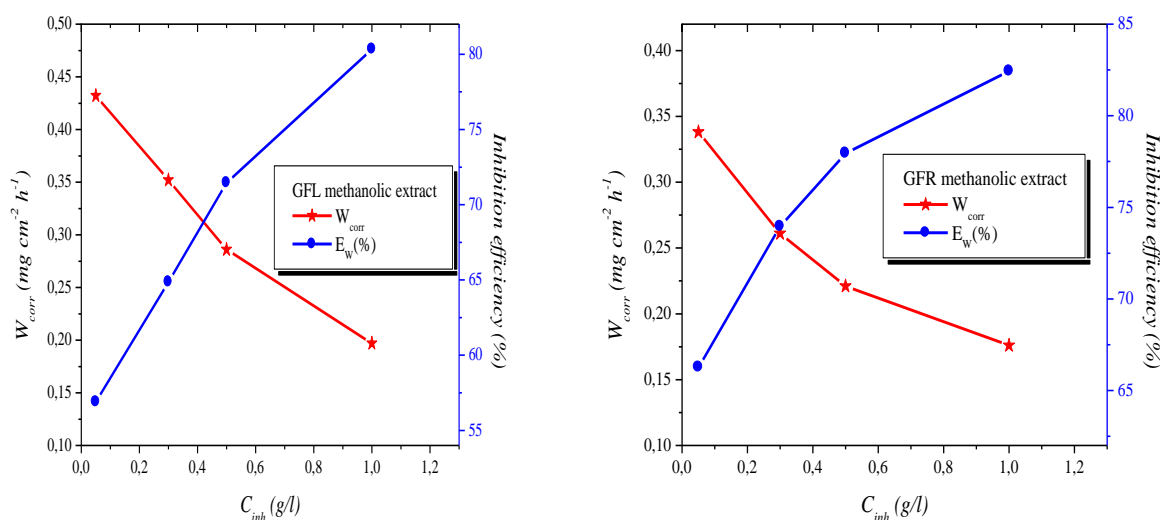


Figure.1 Corrosion rates and inhibition efficiencies obtained at different concentrations of both methanol extracts in 1.0 M HCl at 298K for 6h.

3.2. Adsorption isotherm and thermodynamic

The action of an inhibitor in aggressive acid media is assumed to be due to its adsorption at the metal/solution interface. The adsorption process depends on the electronic characteristics of the inhibitor, the nature of metal surface, temperature, steric effects and the varying degrees of surface-site activity [30, 31]. The type of the adsorption isotherm can provide additional information about the properties of the studied extracts inhibitors. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of the inhibitor must be calculated. In this study, the degree of surface coverage values (θ) for various concentrations of the inhibitor in acidic media have been evaluated from the weight loss measurements and listed in Table.1. Attempts were made to fit the θ values to various isotherms, including Langmuir, Temkin, Frumkin and Flory-Huggins. By far, the best fit is obtained with the Langmuir isotherm. Langmuir adsorption isotherm is described by the following equations:

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

By rearranging this equation, where C_{inh} is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant and θ is the surface coverage:

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

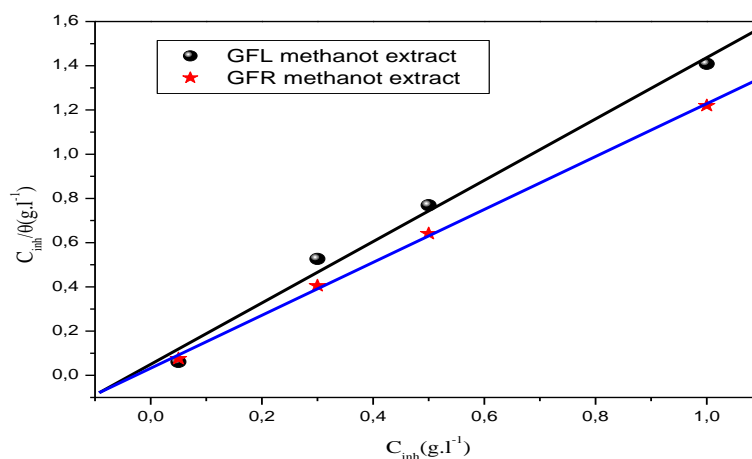


Figure.1. Langmuir adsorption of GFL and GFR methanol extracts on the carbon steel surface in 1.0 HCl solution.

Figure.1 shows the plots of C_{inh}/θ versus C_{inh} and the expected linear relationship is obtained for GFR and GFL methanol extracts. The strong correlations ($R^2 = 0.99$) confirm the validity of this approach. The value of K_{ads} the slope of the straight line (Table.1) suggesting that the adsorbed inhibitor molecules of the methanol extracts form monolayer on the carbon steel surface and there is no interaction among the adsorbed inhibitor molecules[32]. On the other hand, the relatively high value of adsorption equilibrium constant reflects the high adsorption ability of both methanol extracts of grapefruit on carbon steel surface [33, 34]. We suggest that the methanol extract contains a large number of active substances are extracted from GFR and GFL of grapefruit plant with methanol that are more than that in the case of aqueous extract, since it is possible that adsorb some small molecules on mild steel surface followed by adsorption of flavonoid compounds and alkaloids of large size[35]. Generally, for values of ΔG_{ads}° around -20 kJ mol^{-1} or less negative, the type of adsorption is regarded as physisorption; those around -40 kJ mol^{-1} or more negative are associated with chemisorption [36-38]. However, it is difficult to distinguish between chemisorption and physisorption only based on these criteria, especially when charged inhibitors are adsorbed. The possibility of

Coulomb interactions between adsorbed cations and specifically adsorbed anions can increase the Gibbs energy even if no chemical bond appears [39]. However, the calculation of the ΔG_{ads}° value of GFL and GFR methanol extracts is not possible because the molecular mass of the extracts components is not known [19]. This limitation is noted by some authors in the case of the plant extracts used as corrosion inhibitors for steel in acidic media [40, 41].

Table.2: Thermodynamic parameters for the adsorption of GFR and GFL methanol extracts in 1.0 M HCl on the carbon steel at 298K.

Inhibitor	Slope	K_{ads} (g.L ⁻¹)	R^2
GFR	1.19	31.07	0.99
GFL	1.38	20.06	0.99

3.3. Electrochemical impedance spectroscopy measurements (EIS)

Figure 2 shows the electrochemical impedance diagrams in the Nyquist plane Z response of carbon steel in 1.0M HCl medium with and without different concentration of the both studied extracts inhibitor, after 15 minutes of immersion at the temperature 298K and in the frequency range of 1 MHz to 100 kHz. Nyquist impedance plots were analyzed by fitting the experimental data to a simple circuit model (Figure2). Thus, the equivalent circuit depicted in Figure 3 is employed to analyze the impedance spectra, where R_s represents the solution resistance, R_t denotes the charge-transfer resistance, and C_{dl} represents the interfacial capacitance. The values of the interfacial capacitance C_{dl} can be calculated from equation, where f_{max} is the frequency value at which the imaginary component (Z_{im}) of impedance is maximum:

$$C_{dl} = (2\pi \cdot f_{max} \cdot R_t)^{-1}$$

The inhibition efficiency can be calculated by the following formula, Where 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 .3

$$E_{RT} \% = \frac{(R_t - R_t^{\circ})}{R_t} \times 100$$

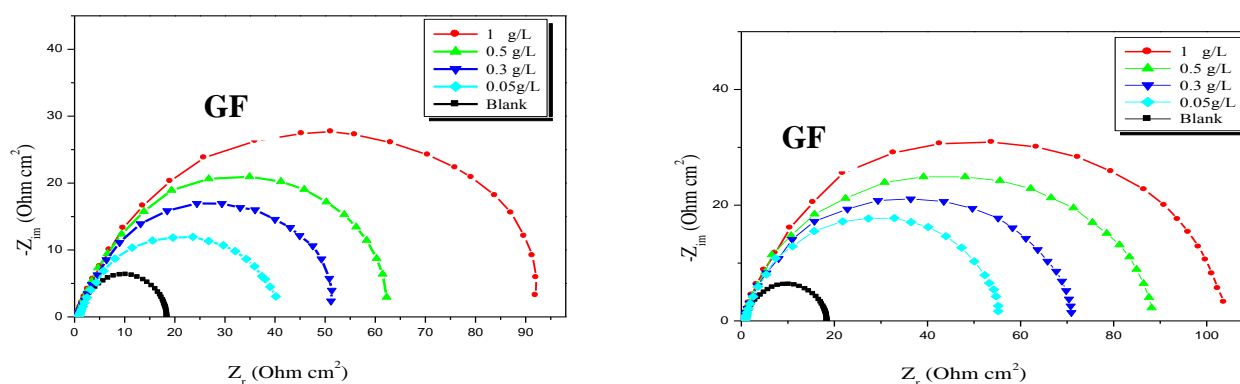


Figure.2: Nyquist plots for carbon steel immersed in 1.0 M HCl solution in the absence and presence of various concentrations of GFR and GFL methanol extract at E_{corr} after 15 min of immersion

All the obtained plots show only one capacitive loop, and the addition of GFR and GFL methanol extract at the solution leads to the increase of the size of the impedance spectrum in the form of a semi-circle at least more flattened

characterizing the formation of a double layer capacitance C_{dl} , which decreases with increasing inhibitor concentration. This result suggests the protective film formation which result from the addition of the methanol extracts [42]. The presence of the inhibitor increases the impedance but does not change other aspects of the behavior. Inspection of the Table 2 shows that the presence of both GFR and GFL methanol extract enhances the charge transfer resistance R_t which is attributed to a decrease in local dielectric constant and/or an increase in the thickness of electrical double layer [43]. % IE obtained from this technique is also comparable with those obtained from polarization measurements.

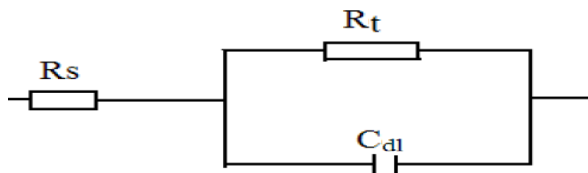


Figure.3: Equivalent circuit diagram

Table.3: Data from electrochemical impedance spectroscopy measurements of carbon steel in 1.0M HCl solution in the absence and presence of various concentrations of the inhibitors.

Inhibitor	Concentration (g/L)	R_t ($\Omega \cdot \text{cm}^2$)	C_{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	E_{RT} (%)
Blank	0.0	18	221	-
GFL	1.00	92	115	80,43
	0,50	66	161	72,73
	0,30	52	204	65,38
	0,05	42	253	57,14
	1.00	105	101	82.86
GFR	0.50	83	128	78.31
	0.30	70	152	74.29
	0.05	55	193	67.28

3.4. Potentiodynamic Polarization curves

Figure.4 represents the anodic and cathodic polarization curves of carbon steel electrode in 0.1 M HCl solutions devoid of and containing different concentrations of GFL methanol extract. Similar curves were obtained for the GFR methanol extract (not shown) but their corrosion parameters are given in Table 4. More electrochemical parameters, i.e., the corrosion potential (E_{corr}), the corrosion current density (I_{corr}) and the anodic (β_a) and cathodic (β_c) constants, shown in Table 4, were obtained by fitting the Tafel plots. Inspection of this figure reveals that the polarization curves shift toward more negative potential and lower current density values upon the addition of the methanol extract. This behavior reflects the inhibitive action of GFL methanol extract. The corrosion parameters of carbon s electrode in the free and inhibited 0.1M HCl solutions were obtained from the curves of Figure.4 and given in Table 4.

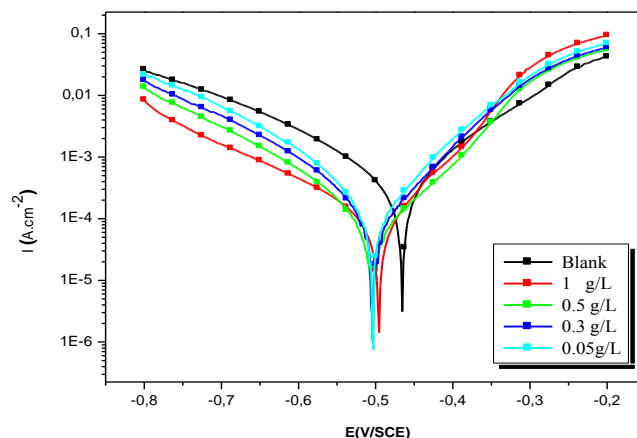


Figure.4: Potentiodynamic polarization curves for carbon steel immersed in 1.0M HCl solution in the absence and presence of various concentrations of GFL methanol extract

Table.4: Data obtained from potentiodynamic polarization measurements of carbon steel immersed in 1.0M HCL solution in the absence and presence of various concentrations of the tow methanol extracts.

Inhibitor	Concentration (g/L)	$-E_{\text{corr}}$ (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	$-\beta_c$ (mV/dec)	Ba (mV/dec)	E_i (%)
Blank	0	463	636	168	123	-
GFL	1.00	496	161	128	72	79,89
	0.50	506	141	178	74	72,01
	0.30	503	155	224	74	64,78
	0.05	501	158	274	78	56,92
GFR	1.00	485	152	121	81	80,97
	0.50	497	140	137	70	78,46
	0.30	504	132	168	63	73,56
	0.05	514	125	209	75	67,13

The data in *Table 4* show that the corrosion potential shifts to more negative values as the concentration of added methanol extract is increased. The corrosion potential varies with the concentration of the extract, confirming the mixed nature of both methanol extracts [18-19]. Moreover the corrosion current density decreases markedly on addition of the methanol extract indicating the inhibiting effect of these methanol extracts. The decrease in the density of the corrosion current is due to the active site blocking effect on the metal surface by adsorbed molecules of the methanol extracts [44.] and consequently slowing the corrosive process.

This result reveals that the inhibitors adsorbed to the carbon steel electrode could modify the metal dissolution reaction. The inhibition efficiency calculated from the I_{corr} values obtained in the absence and presence of methanol extracts increases with increasing extract concentration which is proposed to be an insoluble complex adsorbed on mild steel surface, leading to more inhibition efficiency with increasing the concentration of the extract under study,

this complex lead to block most of the active centers on mild steel surface, thereby increasing the surface coverage [45].

$$E_i \% = \left(1 - \frac{I_{corr}}{I_{corr}'}\right) \times 100$$

3.5. Thermodynamic activation parameters

To calculate the activation parameters of the corrosion process, EIS measurements were obtained at different temperatures in the absence and the presence of both GFL and GFR methanol extracts and precisely in the range of temperature 298-328 K. These parameters are useful in interpreting the type of adsorption by the inhibitors. EIS measurements parameters are listed in the Table 5.

Table.5: 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	-
GFL	298	92	115	80,43
	308	60	265	81,67
	318	39	272	79,49
	328	26	408	80,77
GFR	298	105	117	82.86
	308	68	152	83.82
	318	42	153	80.95
	328	26	117	80.77

In the temperature range studied (298–328K) the values of R_t decrease with increasing temperature both in uninhibited and inhibited solutions and the efficiency of inhibition by GFR and GRL extracts decreases slightly with increasing temperature. In short, that the temperature had no effect on the inhibitors efficiency. To study the adsorption mechanism of both methanol extracts, 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 [46 -47]:

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

Where R is the universal gas constant ($R = 8.31 \text{ J K}^{-1}\text{mol}^{-1}$), T is the absolute temperature, z is the valence of iron ($z = 2$), F is the Faraday constant ($F = 96485 \text{ coulomb}$) and R_t is the charge transfer resistance.

Many authors [20, 46-47] use the Arrhenius equation to account for the effect of temperature (T) on the rate of corrosion and therefore consider that the logarithm of the corrosion rate I_{corr} is a linear function of the inverse of the temperature ($1/T$):

$$I_{corr} = A \exp\left(-\frac{E_a}{RT}\right)$$

In this relation E_a represents the apparent activation corrosion energy, R is the perfect gas constant, T the absolute temperature and A the pre-exponential parameter of Arrhenius. To predict the inhibition mechanism, the activation energy for the corrosion reaction in the absence and presence of various concentrations of grapefruits methanol extracts at temperatures ranging between 298K and 328K was evaluated by the fitting the logarithm of the corrosion rate of carbon steel I versus $1000/T$ (Figure.5).

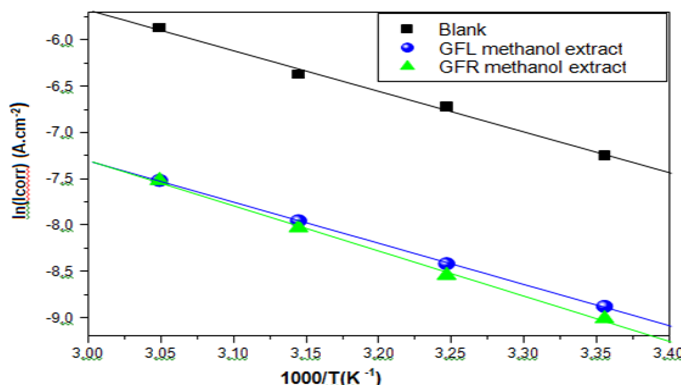


Figure 5: Arrhenius plots of carbon steel in 1.0 M HCl with and without 0.5 g/L of both methanol extracts.

The values of the apparent activation energies obtained from the slope of the lines for the different concentrations of both methanol extracts and at different temperatures are grouped in Table 5. The adsorption mechanism of organic inhibitors on metal surfaces can be by physical adsorption or chemical adsorption; and is influenced by factors such as nature of the charge of the metal, the chemical structure of the inhibitor, pH, the type of electrolyte and temperature [48]. The variation of the E_a values can be attributed to the positions of the inhibitor molecules on the metal surface [59, 50]. This observation confirms the mechanism of physisorption of the methanol extracts on the carbon steel as the work of several researchers shows [50-54]. Activation parameters, such as entropy and enthalpy of corrosion process, may be evaluated from the effect of temperature. An alternative formulation of Arrhenius equation [46-47]:

$$I_{corr} = \frac{RT}{Nh} \cdot \exp\left(\frac{\Delta S^*}{R}\right) \cdot \exp\left(-\frac{\Delta H^*}{RT}\right)$$

Where N is the Avogadro's number, h the Plank's constant, R is the perfect gas constant, ΔS^* and ΔH^* the entropy and enthalpy of activation, respectively. Fig. 6 shows a plot of $\ln(I_{corr}/T)$ against $1/T$ for the GFR and GFL methanol extracts. Straight lines are obtained with a slope of $(-\Delta H^*/R)$ and an intercept of $(\ln R/Nh + \Delta S^*/R)$ from which the values of ΔH^* and ΔS^* are calculated and listed in Table 5.

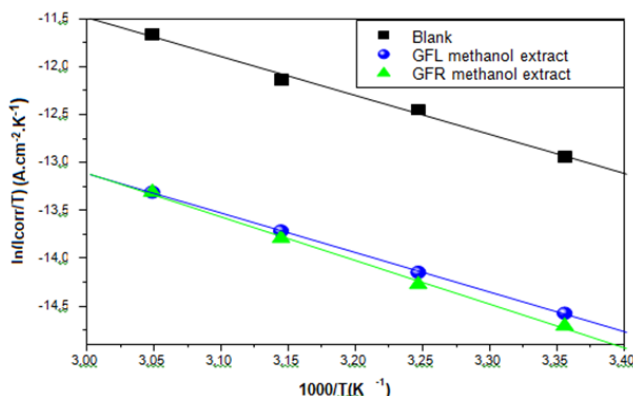


Figure 6: Relation between $\ln(I_{corr}/T)$ and $1000/T$ in acid at different temperatures in the absence and presence of 0.5 g/L of GFR and GFL methanol extracts.

Table 5: The value of the kinetic parameters for carbon steel in 1.0 M HCl in 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
GFL	34.28	-203.59	36.87	2.60
GFR	37.88	-192.77	40.47	2.60

Analysis of the values listed in Table 5 shows that the values of the activation enthalpy ΔH^* of the dissolution reaction of carbon steel in 1M HCl in the presence of the tow methanol extracts are greater compared to the case of the free acid. The positive sign of these enthalpies reflects the endothermic nature of the carbon steel dissolution process. The high and negative values of the entropy ΔS^* imply that the active complex in the speed determining step represents an association rather than a dissociation, meaning that there is a decrease in the disorder during the transformation of the reagents into Activated complex[55-56].

3.6. Optical microscopy (OM)

Optical microscopy images were recorded to investigate the changes occurred on the surface of the carbon steel samples after 6 hours immersion in 1.0 M HCl solution in the absence and presence of the both methanol extracts (Fig. 7). Fig. 7b presents the micrograph obtained for a carbon steel sample after exposure to blank solution carbon we can see that the carbon steel surface in the uninhibited solution is severely damaged and rough was a characteristic of the uniform corrosion of carbon steel in acid medium. Fig.7c and Fig.7d shows a smooth surface can be observed, indicating that the surface was covered by inhibitors, reveals that the corrosion marks on the inhibited samples decrease in presence of *GFL* and *GFR* methanol extracts respectively, which also attests the inhibition ability and adsorption of the inhibitor on the carbon steel surface. This is attributed to the formation of a good protective film on the carbon steel surface. Moreover, the appears lines on the carbon steel surface can be attributed to polishing scratches.

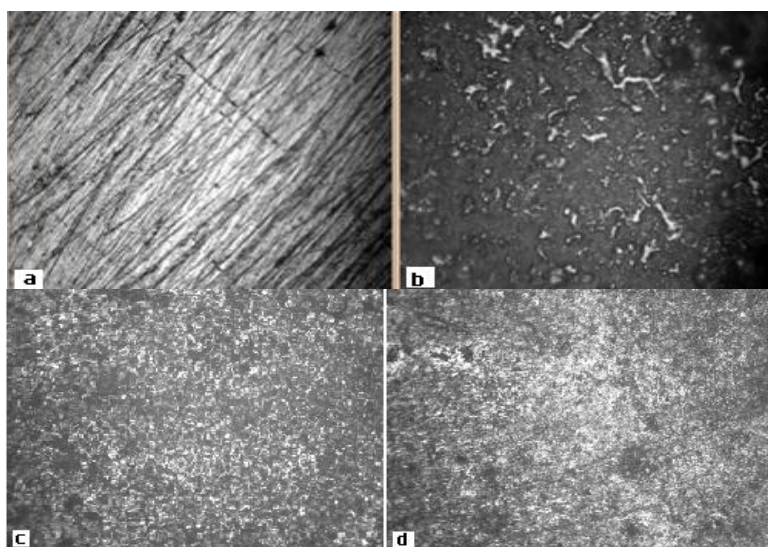


Figure 7: shows a OM micrograph of carbon steel surface before immersion Fig.7a), after 6h of immersion in 1.0 M HCl in the absence (Fig. 7b) ,the presence of 0.5g/L of methanol *GFL* extracts (Fig. 7c) and the presence of 0.5g/L of methanol *GFR* extract (Fig. 7d) at 298K.

4. Conclusion

The inhibitory effect of the two extracts on the corrosion resistance of steel in acid medium was quantified by weight loss measurements and using potentiodynamic polarization curves. The electrochemical results of polarization also showed that both methanol extract of grapefruit acts as mixed type inhibitors, those retarded both cathodic and anodic reaction. The action of these two extracts is based on a simple mechanism of adsorption on the surface of the metal, thus blocking the active sites and consequently decreasing the densities of corrosion currents. The adsorption of these extracts to the metallic surface led to the formation of a protective film of monolayer type and follows the Langmuir adsorption isotherm. These results are confirmed by OM micrograph of carbon steel surface. We can deduce from the experimental results that the GFR methanol extract was more physical adsorption than that of the GFL methanol extract by forming a protective film that is more adherent and therefore more effective than the GFR methanol extract.

Reference

- [1] Hussin M. H., Kassim M. J., *Materials Chemistry and Physics*, 125 (2011) 461–468.
 - [2] Eddy N. O., Odoemelam S. A. and Mbaba A. J., *Afri. J. Appl. Chem.* 2(12) (2008c) 132-138.
 - [3] Ebenso E.E. and Ekpe U. J., *W. Afri. J. Biol & Appl. Chem.* 41(1996) 21-27.
 - [4] Eddy N.O., Odoemelam S.A., Odiongnyeni A.O., *Journal of applied electrochemistry*, 39 (6)(2009) 849-857
 - [5] Ogunzie E. E., Ogunkwe B. N., Okolu B. N., Onuoha G. N. and Onuchukwu A. I., *Materials Chemistry and Physics* 87 (2), 394-401
 - [6] Abiola O. K., Tobun Y., *Chinese Chemical Letters*, 21 (2010) 1449–1452
 - [7] Vasanth, Vasanth, K.L. NACE. National Association of Corrosion Engineers, Paper# 233, Corrosion (2009) 96.
 - [8] Hui-Long W., Hong-Bo F., and Jia-Shen Z., *Materials Chemistry and Physics* 77 (2003) 655.
 - [9] Abiola O. K., Oforka N. C., Ebenso E. E., Nwinuka N. M., *Anti-Corrosion Methods and Materials*, 54(4) (2007).
 - [10] Uwah I.E., Okafor P.C., Ebiekpe V.E., *Arabian Journal of Chemistry*, 6 (2013) 285–293
 - [11] Nnabuk O. Eddy, Femi Awe and Eno E. Ebenso, *Int. J. Electrochem. Sci.*, 5 (2010) 1996 – 2011
 - [12] Odiongnyeni A.O., Odoemelam S.A., Eddy N.O., *Portugaliae Electrochimica Acta*, 27(1) (2009) 33-45.
 - [13] Nnabuk Okon Eddy, *International Journal of Physical Sciences*, 4 (4) (2009) 165-171.
 - [14] Eddy N. O., Mamza P. A. P., *Portugaliae Electrochimica Acta*, 27(4) (2009) 443-456.
 - [15] Achebe C.H., Ilogebe A. B, Chukwuneke J. L., Azaka O. A., Ugwuegbu D. C., *The International Journal Of Engineering And Science (IJES)*, 4(10) (2015) 01-09.
 - [16] Eddy N. O., Odoemelam S. A., and Ama I. N., *Green Chemistry Letters and Reviews*, 3(3) (2010) 165-172.
 - [17] Amitha Rani B. E., and Bharathi Bai J. Basu, *Hindawi Publishing Corporation International Journal of Corrosion*, (2012), doi:10.1155/2012/380217.
 - [18] Khoudali S., Benmessaoud D., Essaqui A., Zertoubi M., Azzi M., Benaissa M., *J. Mater. Environ. Sci.* 5 (3) (2014) 887-898.
 - [19] Salhi A., Bouyanzer A., El Mounsi I., Hamdani I., Bendaha H., Rmili R., Akichouh H., Allali M., Zarrouk A., Hammouti B., Costa J., *Der Pharmacia Lettre*, , 8 (2) (2016) 33-42.
 - [20] Ben Hmamou D., Salghi R., Bazzi Lh., Hammouti B., Al-Deyab S.S., Bammou L., Bazzi L., Bouyanzer A., *Int. J. Electrochem. Sci.* 7 (2012) 1303 – 1318.
 - [21] Ben Hmamou D., Salghi R., Zarrouk A., Hammouti B., Al-Deyab S.S., Bazzi Lh., Zarrok H., Chakir A., Bammou L., *Int. J. Electrochem. Sci.* 7 (2012) 2361 – 2373.
 - [22] Archana S., Anurag S., Deepti S., Praveen J., *E-Journal of Chemistry*. 9(4) (2012) 2044
- Mor. J. Chem.* 5 N°3 (2017) 404-416

- [23] Ating E.I., Umoren S.A., Udousoro I.I., Ebenso E.E., Udoh A.P., *Green Chem. Let. Rev.* 3(2) (2010) 61
- [24]. Senhaji B., Ben Hmamou D., Salghi R., Zarrouk A., Chebli B., Zarrok H., Warad I., Hammouti B., Al-Deyab S. S., *Int. J. Electrochem. Sci.* 8 (2013) 6033 – 6046.
- [25] Leelavathi S., Rajalakshmi R.; *J. Mater. Environ. Sci.* 4 (2013) 625-638.
- [26] Dahmani M., Al-Deyab S.S., Et-Touhami A., Hammouti B., Bouyanzer A., Salghi R., ElMejdoubi A., *Int.J. Electrochem. Sci.* 7 (2012) 2513 – 2522
- [27] Singh A. , Ishtiaque A. , Singh V. K., Quraishi M.A., *J Solid State Electrochem.* 15 (2011) 1087–1097
- [28] Singh A., Singh V. K., Quraishi M. A., *J. Mater. Environ. Sci.* 1 (3) (2010) 162-174.
- [29] A M. Abdel-Gaber, M. S. Masoud, E A. Khalil, E. E .Shehata., *Corros. Sci.* 51 (2009) 3021.
- [30] El-Awady A. A., Abd-El-Nabey B. A., Aziz S. G., *J. Electrochem. Soc.* 139 (1992) 2149.
- [31] Bockris J.O'M., Reddy A.K.N., *Modern Electrochemistry*, vol. 2, Plenum Publishing Corporation, New York, (1976).
- [32] Ebenso E. E., Obot I.B., Murulana L C., *Int. J. Electrochem. Sci.* 5 (2010) 1574.
- [33] Migahed M. A., *Mater. Chem. Phys.* 93 (2005) 48.
- [34] Wang X., Yang H., Wang F., *Corros. Sci.* 53 (2011) 113.
- [35] Aisha M. Al- Turkustani, Sanaa T. Arab , Areej A. Al- Reheli, *International Journal of Chemistry*, 2 (2) (2010)
- [36] Bahrami M.J., Hosseini S.M.A., Pilvar P., *Corros. Sci.*, 52 (2010) 2793.
- [37] Behpour M., Ghoreishi S.M., Mohammadi N., Soltani N., Salavati-Niasari M., *Corros. Sci.* 52 (2010) 4046.
- [38]. Ehteshamzadeha M., Jafari A.H., Naderia E., Hosseini M.G., *Mater. Chem. Phys.*, 113 (2009) 986.
- [39] Singh A.K., Quraishi M.A., *Corros. Sci.* 53 (2011) 1288.
- [40] Lebrini M., Robert F., Roos C., *Int. J. Electrochem. Sci.* 6 (2011) 847.
- [41] Faustin M., Maciuk A., Salvin P., Roos C., Lebrini M., *Corros. Sci.* 92 (2015) 287.
- [42] Amar H., Braisaz T., Villemain D., Moreau B., *Mater. Chem. Phys.*, 110 (2008) 1.
- [43] Quraishi M. A., Singh A., Singh V. K., Yadav D. K., Singh A. K., *Mater. Chem. Phys.*, 122 (2010) 114.
- [44] Li X., *Corros. Sci.* 51 (2009) 620-634.
- [45] Aisha M. Al- Turkustani, Sanaa T. Arab , *International Journal of Chemistry*. 2(2) (2010) 54-76.
- [46] Anejjar A., Salghi R., Zarrouk A., Benali O., Zarrok H., Hammouti B., Ebenso E. E.. *J. Assoc. Arab. Univer Bas & Appl Sci.* 15 (2014) 21.
- [47]. Bousskri A., Anejjar A., Lgaz H., Belkhaouda M., Jodeh S., Hammouti B., *Appl. J. Envir. En. Sci.* 1 (1) (2015) 9-24
- [48] Benabdellah M., Aouniti A., Dafali A., Hammouti B., Benkaddour M., Yahyi A., Ettouhami A., *Appl. Surf. Sci.*, 2006, 252, doi: 8341.10.1016/j.apsusc.2005.11.037.
- [49] Tebbji K., Faska N., Tounsi A., Oudda H., Benkaddour M., Hammouti B., *Mater. Chem. Phys.* 106 (2007) 260–267.
- [50] Behpour M., Ghoreishi S.M., Khayatkashani M., Soltani N., *Mater. Chem. Phys.* 131(2012) 621-633.
- [51] Kamal C., Sethuraman M.G., *Arabian Journal of Chemistry*. 5 (2012) 155–161.
- [52] Lebrini M., Robert F., Lecante A., Roos C., *Corros. Sci.* 53 (2011) 687-695.
- [53] El-Etre A.Y., Abdallah M., El-Tantawy Z.E., *Corrosion. Sci.* 47 (2005) 385–395
- [54] Hodaifa G., Ochando-Pulido J.M., Ben Driss Alami S., Rodriguez-Vives S., Martinez-Ferez A., *Ind.Crop.Prod.* 49 (2013) 526– 534.
- [55] Marsh J., *Advanced Organic Chemistry*, 3rd Edition, Wiley Eastern, New Delhi, (1988).
- [56] Martinez S., Stern I., *Appl. Surf. Sci.* 199 (2002) 83.