



Corrosion inhibition by naturally occurring substance containing *Opuntia-Ficus Indica* extract on the corrosion of steel in hydrochloric acid

Z. Ghazi¹, H. ELmssellem¹, M. Ramdani¹, A. Chetouani^{1,2}, R. Rmil¹, A. Aouniti¹, C. Jama³
and B. Hammouti^{1*}

¹Laboratoire de Chimie Appliquée et environnement (LCAE-URAC18), Faculté des Sciences, Oujda, Morocco

²Laboratoire de chimie physique, Centre Régionale des Métiers de l'Éducation et de Formation "CRMEF", Région de l'Orientale, Oujda, Morocco

³UMET-ISP, CNRS UMR 8207, ENSCL, Université Lille Nord de France, F-59652 Villeneuve d'Ascq Cedex, France

ABSTRACT

Corrosion is an unavoidable but a controllable process. Due to the issues of toxicity of substances, there is an increasing interest in exploration and utilization of eco-friendly inhibitors, which are also known as green inhibitors. The inhibitive effects of aqueous extracts of *Opuntia ficus indica* (OFI) on the corrosion of mild steel, in hydrochloric acid have been investigated by weight loss and polarisation measurements. Weight loss measurements gave an inhibition efficiency of about 91 % in the presence of 5g/l at 308K. EIS results revealed that green inhibitor effects excellently as a corrosion inhibitor for C38 steel in 1 M hydrochloric acid media with retarded the dissolution reactions to an extent dependent on the metal used. Polarisation measurements indicate that all the extracts increase the polarisation of the cathodic reaction of all the steel tested and the anodic polarisation, have no effect on the anodic reaction. The above results showed that OFI acted as a mixed-type corrosion inhibitor and the mechanism of inhibition has been discussed. The changes in impedance parameters (charge transfer resistance, R_{ct} , and double layer capacitance, C_{dl}) were indicative of adsorption of OFI on the steel surface, leading to the formation of protective films. The adsorption of used compound on the steel surface obeys Langmuir's isotherm. The apparent activation energy, enthalpy of the dissolution process and the free energy were determined and discussed.

Key words: steel, inhibition, corrosion, hydrochloric acid, Green inhibitors, Plant extracts, *Opuntia ficus indica*

INTRODUCTION

The prickly pear, *Opuntia ficus-indica*: (OFI), is a species of plant of the family Cactaceae, is widely distributed in Morocco, native to Mexico, and cultivated in dry regions as an important nutrient and food source. It's a highly productive cactus, which is cultivated as a food source for both human and animals. Also, it plays an important ecological part in combating erosion, and it is adapted and integrates in the agricultural production system of arid and semi-arid zones in Morocco. This is an interesting vegetable due the environmental conditions in which it grows and its resistance to climatic extremes; however, little is known about its nutritional properties, especially in the later stages of maturity. The *Opuntia ficus-indica* (OFI) fruit is an important and abundant potential raw material for the Moroccan industry where they play a strategic role in subsistence agriculture and the cactus cladodes, fruits, and flowers are traditionally used as medicines in several Countries, The *Opuntia Ficus Indica*: 58.79%. Linoleic acid was the dominating fatty acid with an exceptional level, up to 58.79% for OFI oil. OFI contained a higher amount of sterols: 27.32% in total lipid oil. These results bring attention to the possible use of cactus seed oil as a natural source of PUFA for nutritional, industrial or pharmaceutical purpose [1, 3].

Opuntia prickly pads are an important source of several nutritional elements like pectin, mucilage and minerals. Currently there is only information related to young stage pads and precious little relating to the nutritional value of

older maturity stage pads. The fresh young pads, also known as cladodes, are an excellent source of proteins including essential amino acids, and vitamins. Several studies have reported that high levels of amino acids, especially proline, taurine and serine can also be found in prickly pads [4-6].

In contrast, not much information is available about the older prickly pads regarding their amino acid profiles. Also noteworthy is the fact that there is a gap in studies that have already been published regarding. The nutritional importance of cactus pear fruit juice is mainly due to the content of sugars, ascorbic acid, fibres and free amino acids (particularly proline, glutamine and taurine). Other components are present such as lipids, phenolics, proteins, organic acids and minerals include calcium, potassium, and magnesium. The fruit juice is also characterised by a high content of betalain, a widely used natural colorant in the food industry. The fruits are used for the manufacture of food products such as juices [7], alcoholic beverages [8], jams [9] and natural liquid sweeteners [10]. One of the more valuable contributions of cactus fresh fruits to a diet is their vitamin C content. In addition to their nutritional properties, these plants contain biocompounds with several commercial applications [4]. One such compound is betalain, a water-soluble nitrogen-containing pigment. It is found in high concentrations in cactus pear plants [11,12] in the form of betalamic acid, which is the chromophore common to all betalain pigments [13] used as natural food colorants [14-15]. The most important biocompounds in cactus fruit are phenolic compounds [16], betacyanins, and betaxanthin pigments, all of which have potent antioxidant properties [17,18]. Phenolic compounds can be defined as substances possessing an aromatic ring, carrying one or more hydroxyl groups, including their functional derivatives [19]. The chemical structure and concentration are quite variable and depend on the variety, ripening stages, and the kind of plant tissue [20]. Glycosylated flavonols, dihydroflavonols, flavonones and flavonols have been found in Cactaceae plants and fruits [21].

Metals are the pre-eminent important materials used in structural and decorative applications. The corrosion, deterioration or destruction of metals is an unavoidable but controllable process. Specially, the steel is the most commonly used metallic material in all industrial process, due to its low cost. Unfortunately it is a subject of corrosion phenomena that become important particularly in acidic media. This is the reason that a development of protection systems is an important issue.

The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that have biocompatibility in nature. The inhibitors like plant extracts presumably possess biocompatibility due to their biological origin. Similar to the general classification of “inhibitors”, “green inhibitors” can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors. The use of corrosion inhibitors is one of the most cost effective methods. Therefore a development of safe corrosion inhibitors called “environmentally friendly corrosion inhibitors” is required. An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties [22-30].

Corrosion inhibitors are widely used in concrete, where conventional formulations often include species that have significant toxicity. As a result, they are being scrutinized by environmentalists and could be stopped from being used in the near future since they are significant biohazards and pollutants.

The use of these natural products such as extracted compounds from leaves or seeds as corrosion inhibitors have been widely reported by several authors. Recently, several studies have been carried out on the inhibition of corrosion of metals by plant extract are used as common corrosion inhibitors. Shauhan and Gunasekaran [31] studied the corrosion inhibition of steel by eco-friendly *Zenthoxylum alatum* plant extract in HCl as well as in phosphoric acid medium. Essential oils and leaves extracts are used as common corrosion inhibitors. The anticorrosion activity of leaves extracts as henna [32], *Artemisia* [33-35], pepper [36], lavender [37], and *Accacia conicianna* [38] was investigated. Corrosion inhibition has also been studied for the essential oils and extracts of *lawsonia* [39]. Similar results were also shown by *Rosmarinus officinalis* [40], *Annonas quamosa* [41], *Acacia Arabica* [42], *Carica papaya* [43], *Azadirachta indica* and *Vernonia amydalina* which were used for steel in acid media. *Nyfafructicans wurmb* leaves were studied for the corrosion inhibition of mild steel in HCl media [43-46].

However, the use of the prickly pear (OFI) extract as a corrosion inhibitor is limited. In the literature, few studies have been carried out recently in various conditions and indicated an excellent protective effect. Hammouch *et al.* [47] showed an important inhibition efficiency about 86% of the *Opuntia* extract, toward corrosion of iron in 3% sodium chloride. In an interesting study investigated by El-Etre, [48] the inhibition action of the mucilage extracted from the modified stems of prickly pears toward acid corrosion of aluminium, acts a good corrosion inhibitor for aluminium corrosion in 2.0 M HCl solution. The inhibition efficiency attained 96%. More recently, Salghi *et al.* [49] showed that a high efficiency 90 % was obtained at 5 g/L of a Prickly pear seed oil extract tested as corrosion

inhibitor for mild steel in 1M HCl. The study carried by Chtaini *et al.* [50] showed that the pigment extracted from reddish prickly pear juices act as a good inhibitor for 316L stainless steel in 30% H₃PO₄ solution. The inhibition efficiency of pigment extracts increases with the concentration to attain a maximum value 97% at 1mL of pigment extract. Recently, an important product patented in Morocco [51] by Hammouch *et al.*, [52] based on fatty acid of (OFI), triethanolamine and KOH indicated an excellent protective effect. The inhibiting efficiency attained 98.8% when 0.05% of the product was added.

The aim of this study was to study the inhibitive action of the fruit juice of (OFI) on corrosion behaviour of mild steel in 1M HCl by gravimetric method and electrochemical techniques such as potentiodynamic polarisation, linear polarisation and electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL SECTION

2.1. Preparation of *Opuntia Ficus indica* extract

The fruits of the prickly pear (*Opuntia ficus indica*) (Figure 1) were collected in June 2013 in the region of Oujda (Morocco). They were washed and husks removed in the laboratory in order to recover the fruit pulp, what dotted with several small seeds. The pulp is mixed for five minutes in a blender, then passed through a sieve for separating the seeds from the juice.

Thereafter, the juice is dried in a stove at 40 °C. The analysis determined the proportion of various molecules in the peels presented higher yields in total phenolic compounds and flavonoids followed. Evaluation activity of the extract, showed better reduction potential and the inhibitory effect of OFI.



Figure 1: *Opuntia Ficus Indica*; a) plante, b) fruit

2.2. Weight loss measurements

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100ml. The steel specimens used have a square form (1.5cm x 1.5cm). Prior to immersion, the iron samples were polished with different emery papers, degreased with acetone washed thoroughly with doubly distilled water, and finally dried in air. The immersion time for the weight loss was 1 hour at different temperatures. The aggressive solutions (1M HCl) were prepared by diluting analytically grade 37% HCl with doubly distilled water. The concentration range of this compound was 0.5 to 5g/l. The chemical composition of mild steel is given in Table1

Table 1: Chemical composition of mild steel.

Elements	Fe	C	Si	P	Mn	S	Al
% en masse	99.21	0.21	0.38	0.08	0.05	0.05	0.01

2.3. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltmaster software. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was the same used for gravimetric measurements. The surface area exposed to the electrolyte is 1 cm².

Potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5 mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from -800 mV to -400

mV at 308 K. The solution test is there after de-aerated by bubbling nitrogen. Gas bubbling is maintained prior and through the experiments. Some tests were carried out in a temperature 308 K.

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), 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. Experiments are repeated three times to ensure the reproducibility.

RESULTS AND DISCUSSION

3.1. Gravimetric measurements

The effect of addition of extracts of *Opuntia ficus indica* tested at different concentrations on the corrosion of C38 steel in 1M HCl solution was studied by weight loss measurements at 308 K after 6 h of immersion period. The corresponding data are shown in Table 3. The corrosion rate (W) was calculated from the following equation:

$$W = \frac{(m_1 - m_2)}{(S.t)} \quad (1)$$

where m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after corrosion, S the total area of the specimen, t the corrosion time and W the corrosion rate.

Values of corrosion rate (W_{corr}°) and inhibition efficiencies (E_w) are given in Table 2. In the case of the weight loss method; the relation determines the inhibition efficiency E_w is determined by the relation (2):

$$E_w \% = \left(1 - \frac{W_{corr}}{W_{corr}^{\circ}} \right) \cdot 100 \quad (2)$$

where W_{corr}° and W_{corr} are the corrosion rates of iron samples in the absence and presence of the naturally substance henna, respectively. The degree of surface coverage (θ) was calculated using equation (3):

$$\Theta = 1 - \frac{W_{corr}}{W_{corr}^{\circ}} \quad (3)$$

Table2. Inhibitor efficiencies for the corrosion of mild steel in 1M HCl for various concentrations of juice fruit *Opuntia Ficus Indica*.

Concentration OFI (g/L)	W (mg/cm ² .h)	E_w (%)	θ
HCl	0.820	--	--
0.5	0.116	85.91	0.86
1	0.102	87.50	0.87
2	0.093	88.64	0.88
3	0.076	90.70	0.90
5	0.068	91.76	0.91

It's clear that the addition of juice fruit *Opuntia Ficus Indica* reduces the corrosion rate in HCl 1M solution. The inhibitory effect increases then with the increase of juice fruit *Opuntia Ficus Indica* concentration. $E\%$ reaches a maximum of 91% at 5g/l for this inhibitor.

We may conclude that juice fruit *Opuntia Ficus Indica*, is a good inhibitor of iron corrosion in 1M HCl solution. It is well known that green inhibitor (OFI) contain numerous organic compounds. It is rather difficult to understand the mechanism of inhibition for a cluster of different compounds present in a plant extract.

3.2. Inhibition efficiency based on electrochemical measurements

In order to get more information about the corrosion behavior of steel, in acidic solution with and without juice of OFI, electrochemical impedance spectroscopy (EIS) measurements have been carried out at 308 K. (Fig. 1) shows polarization curves for C38 steel in 1M HCl without and with different concentrations of juice fruit *Opuntia Ficus Indica*. The electrochemical impedance parameters derived from these investigations are mentioned in Table 3. The

anodic and cathodic current–potential curves were extrapolated up to their intersection point where corrosion current density (I) and corrosion potential (E) are obtained. The electrochemical parameters such as corrosion current density (I), corrosion potential (E), cathodic Tafel slopes (β_c) and inhibition efficiency obtained from polarization measurements are listed in Table 3. In the case of polarisation method the relation determines the inhibition efficiency ($E_i\%$), where I_{corr}° and I_{corr} are the uninhibited and inhibited corrosion current densities,:

$$E_i \% = \left(1 - \frac{I_{corr}}{I_{corr}^{\circ}}\right) \times 100 \quad (4)$$

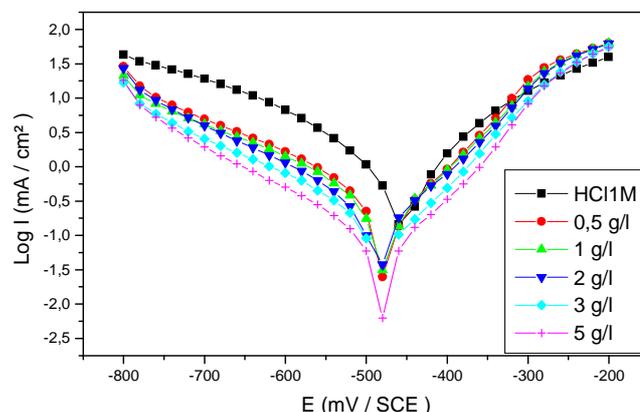


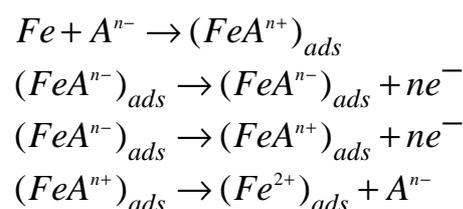
Figure 1. Potentiodynamic polarisation curves of mild steel in hydrochloric acid solution with and without inhibitor at different percentages of juice fruit OFI

Table 3. Potentiodynamic polarisation parameters of the mild steel in HCl solution without and with addition of various juice fruit OFI percentages at 35°C

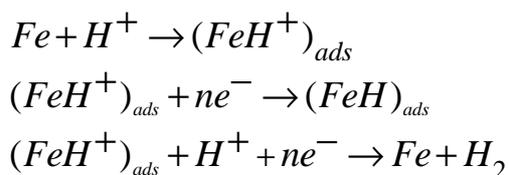
Concentration of OFI (g/L)	E_{corr} (mV/ECS)	$-\beta_c$ (mV/dec)	Ba (mV/dec)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_i (%)
HCl	-455.1	142.8	115.5	666.0	---
0,5	-477.0	183.1	108.3	350.4	47.39
1	-479.4	086.4	088.2	130.1	80.47
2	-486.0	106.0	107.3	118.7	82.18
3	-479.8	134.5	087.2	063.6	90.45
5	-474.6	135.7	085.6	059.4	91.08

It is clear from the results of electrochemical polarisation measurements that the addition of inhibitor causes a decrease of the current density. The values I_{corr} of steel in the inhibited solution are smaller than those for the inhibitor free solution (Table 3). The parallel cathodic Tafel plots obtained in Fig. 1 indicate that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of inhibitor. The change in cathodic Tafel slope (β_c) values (Table 3), suggest that the reaction mechanism of the hydrogen reduction is not the same in the absence and presence of inhibitor.

The inhibiting action is increased with the concentration to reach the maximum value of 91.08% at the 5g/l. The addition of juice fruit *Opuntia Ficus Indica* shifted the E_{corr} value towards the negative direction. A slight effect is observed on anodic curves when curves are compared at $E-E_{corr}$. This indicates that the juice fruit *Opuntia Ficus Indica* acts a mixed inhibitor. The Tafel polarization method confirmed the main weight loss results, giving some additional information. They are determined by extrapolation of Tafel lines to the respective corrosion potentials. Some of the authors proposed the following mechanism for the corrosion of iron and steel in acid solution [53-54]:



The cathodic hydrogen evolution



3.3. Electrochemical impedance spectroscopy (EIS)

The corrosion behaviour of steel in 1M hydrochloric acidic solution, in the absence and presence of OFI, is also investigated by the EIS at 308 K after 30 min of immersion. The charge-transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies. 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:

$$C_{dl} = \frac{1}{\omega \cdot R_t} \quad \text{Where } \omega = 2\pi \cdot f_{max} \quad (5)$$

The inhibition efficiency got from the charge-transfer resistance is calculated by equation (6), where R_t and R'_t are the charge-transfer resistance values without and with inhibitor respectively:

$$E_{Rt} \% = \frac{R'_t - R_t}{R'_t} \times 100 \quad (6)$$

From the impedance data (Table 4), we conclude that the value of R_t increases with presence of the OFI inhibitor and this indicates an increase in the corrosion inhibition efficiency (Fig.2), what is in concord with the electrochemical results obtained

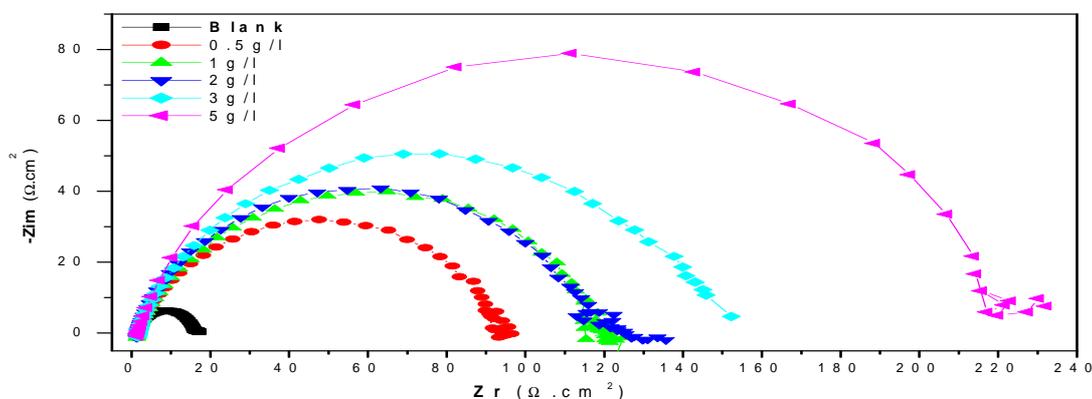


Figure 2. Impedance plot of mild steel obtained in 1M HCl in the absence and presence of various concentrations of OFI

Table 4. Impedance parameters for corrosion of mild steel in hydrochloric acid containing different percentage of OFI

Concentration of OFI (g/L)	R_b ($\Omega \cdot cm^2$)	R_t ($\Omega \cdot cm^2$)	f_{max} (Hz)	C_{dl} ($\mu F/cm^2$)	E_R (%)
HCl	1.370	014.57	54.64	200.0	
0.5	1.587	092.60	31.59	054.44	84.27
1	1.605	117.10	25.52	053.29	87.56
2	1.067	119.70	28.71	046.34	87.83
3	1.381	149.60	24.19	044.01	90.26
5	1.618	219.70	16.88	042.95	93.37

In order to better understand the inhibition mechanism of OFI, a detailed study on this compound was carried out. The impedance parameters are mentioned in table 4. In fact, the presence of inhibitor enhances the value of R_t in acidic solution. 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} follows the order similar to that obtained for I_{corr} in this study. The decrease in C_{dl} is due to the adsorption of this compound on the metal surface leading to the formation of film from acidic solution [32-34,44].

As we notice. Fig. 2, the impedance diagrams show semi-circles whose size increases with the concentration of the inhibitor indicating a charge-transfer process mainly controlling the corrosion of steel. Similar diagrams were described in the literature for the electrode of iron and steel with and without inhibitor 1M HCl [44-53]. From the impedance data (Table 4). the charge transfer resistance (R_t) increases and the double layer capacitance (C_{dl}) decreases with the inhibitor concentration.

3.4. Adsorption isotherm

The primary step in the action of inhibitors in acid solution is generally agreed to be the adsorption on the metal surface. This involves the assumption that the corrosion reactions are prevented from occurring over the area (or active sites) of the metal surface covered by adsorbed inhibitor species, whereas these corrosion reactions occur normally on the inhibitor-free area [52]. Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include Langmuir. Temkin. Frumkin. Hill deBoer. Parsons. Flory-Huggins. Dhar- Flory-Huggins. Bockris-Swinkels and thermodynamic/kinetic model. Adsorption of the inhibitor compounds depends upon the charge and the nature of the metal surface, electronic characteristics of the metal surface on adsorption of solvent and other ionic species, temperature of the corrosion reaction and the electrochemical potential at the metal solution interface [31-34,53].

Adsorption of OFI involves two types of the possible interaction with the metal surface. Inhibitor molecules adsorb on the metal surface if the interaction between molecules and metal surface is higher than that of the water molecule and the metal surface. The first one is weak undirected interaction due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of the metal. This interaction is termed physical adsorption or physisorption. The second type of interaction occurs when there is interaction between the adsorbate and adsorbent. This type of interaction involves charge sharing or charge transfer from adsorbate to the atoms of the metal surface in order to form a coordinate type bond and the interaction is termed chemical adsorption or chemisorptions [30-35]. Accordingly, the fraction of surface covered with inhibitor species (θ) can follow as a function of inhibitor concentration and solution temperature. The surface coverage (θ) data are very useful on discussing the adsorption characteristics. When the fraction of surface covered is determined as a function of the concentration at constant temperature, adsorption isotherm could be evaluated at equilibrium condition. The degree of surface coverage θ for different concentrations of the inhibition in acidic media of different compounds has been evaluated from weight loss using the equation (7):

$$\theta = \frac{W_{(\theta=0)} - W_{\theta}}{W_{(\theta=0)} - W_{(\theta=1)}} \quad (7)$$

The surface coverage values θ were tested graphically for fitting a suitable adsorption isotherm. The plot of C_{inh}/θ versus C_{inh} yields a straight line, proving that the adsorption of the inhibitors from HCl solution on the steel surface obeys the Langmuir adsorption isotherm (Fig. 3) equation (8) and (9) :

$$\frac{C_{inh}}{\theta} = \frac{1}{b} + C_{inh} \quad (8)$$

$$b = \frac{1}{55,5} \cdot \exp\left(-\frac{\Delta G^{\circ}_{ads}}{R.T}\right) \quad (9)$$

C_{inh} is the inhibitor concentration; θ is the fraction of the surface covered. b is the adsorption coefficient and ΔG°_{ads} is the standard free energy of adsorption. Generally, the standard free energy values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption); those of -40 kJ mol^{-1} or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond (chemical adsorption). The obtained plot of inhibitors is linear.

The intercept permit the calculation of the equilibrium constant $b = 0.08086$. which leads to evaluate ΔG°_{ads} (OFI) = -16.74 kJ/mol . The negative values of ΔG°_{ads} indicate the spontaneous adsorption of inhibitors on the steel surface. This value indicates that inhibitor interacts on the steel surface by electrostatic effect. The adsorption mechanism of OFI compounds on C38 steel in 1M HCl solution at the studied temperature is both electrostatic adsorption, which gives maximum efficiency exhibits more negative of ΔG°_{ads} indicating that it is strongly adsorbed on the metal surface [30-32,34]

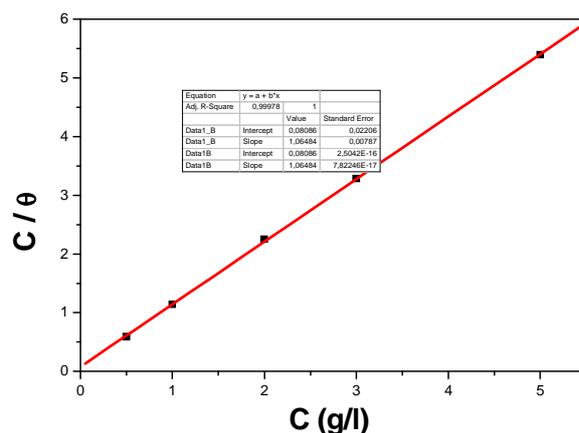


Figure 3. Langmuir isotherm adsorption model of OFI on the steel surface in 1M HCl

CONCLUSION

Generally green inhibitors are excellent inhibitors under a variety of corrosive environments for most of the metals. The non-toxicity and biodegradability are the major advantages for these inhibitors. However, they do have performance boundaries. Although a number of publications are witnessing the green inhibitors as a potential candidate against corrosion at different environments. The following conclusions may be drawn from the study:

- OFI was found to be a good inhibitor of C38 steel corrosion in hydrochloric acid.
- The inhibition efficiency increases with inhibitor concentration to attain a value of 91% (5g/l) at 308 K.
- The adsorption model obeys to the Langmuir adsorption isotherm and was a physisorption.
- Polarisation measurements show that OFI acts a mixed type inhibitor and the impedance method indicates that OFI adsorbs on the C38 steel surface with increasing transfer resistance and decreasing of the double-layer capacitance.
- The inhibitor efficiency determined by electrochemical polarisation, electrochemical impedance spectroscopy and by gravimetric methods are in good agreement.
- Further research efforts are needed to employ the green inhibitors widely at an industrial level.

REFERENCES

- [1] H El Gharras, *Natural Product Communications*, **2011**, 6, 1425-1431
- [2] J Aguirre, TH, De La Garza, CA Zugasti, CR, Belmares, CN Aguilar, *Asian Pac J Trop Biomed*, **2013**, 3(6), 436-442
- [3] Z Ghazi, M Ramdani, M L Fauconnier, B El Mahi, R Cheikh, *J Mater Environ Sci* **2013**, 4(6), 967-972
- [4] J M Feugang, P Konarski, D Z, Florian C Stintzing and C Zou *Frontiers in Bioscience*, **2006**, 11, 2574-2589
- [5] C Saenz, *Journal of Arid Environments*, **2000**, 46, 209-225
- [6] S Jana, *Journal of Engineering Research and Studies*, **2012**, 3(2), 60-66
- [7] M Ennouri, E Bourret, S Baklouti, K Damak, A Rebaï, H Attia, *Sci Aliment* **2006**, 26, 337-348
- [8] EO Bustos, *J Enol Vitic* **1981**, 32, 228-229
- [9] WN Sawaya, HA Khatchadorian, HM Almuhammad, *J Food Technol* **1983**, 18, 183-193
- [10] C Saenz; E Sepulveda *J Prof Assoc Cactus Dev* **2001**, 4, 3-10
- [11] MR Castellar, LM Obón, JA Fernández-López, *J Agric Food Chem* **2003**, 51, 2772-2776
- [9] F Diaz, EM Santos, S Filardo, R villagómez, L Scheinvar, *J Agric Food Chem* **2006**, 5, 1330-1337
- [12] DStrack, T Vogt, W Schliemann, *Recent advances in betalain research Phytochemistry* **2003**, 62, 247-269
- [13] Y Mizrahi, A Nerd, PS Nobel, *Hortic Rev* **1997**, 18, 291-320
- [14] FC Stintzing, A Schieber, R Carle, *Eur Food Res Technol* **2003**, 216, 303-311
- [15] FC Stintzing, R Carle, *Fruit Process* **2006**, 16, 166-171
- [16] JO Kuti, *Food Chem* **2004**, 85, 527-533
- [17] NS Zakharova, TA Petrova, *Prikl Biokhim Mikrobiol* **1998**, 34, 199-202
- [18] C Gentile, L Tesoriere, M Allegra, MA Livrea,; P D'Alessio, *Ann N Y Acad Sci* **2004**, 1028, 481-486
- [19] C Andres-Lacueva, R Zamora-Ros, *J Nutr* **2010**, 103, 307-308
- [20] RS Wallace, *Cactus Succul J* **1986**, 58, 35-38
- [21] JO Kuti, *Hort Sci* **2000**, 35, 433

- [22] H Cang, WY Shi, JL Shao, Q Xu, *Int J Electrochem Sci*, **2012**, 7, 3726-3736
- [23] M Behpour, SM Ghoreishi, M Khayatkashani, N Soltani, *Materials Chemistry and Physics*, **2012**, 131, 621-633
- [24] M Znini, L Majidi, A Bouyanzer, J Paolini, JM Desjobert, J Costa, B Hammouti, *Arabian Journal of Chemistry*, **2012**, 5, 467-474
- [25] S Nofrizal, AA Rahim, B Saad, PB Raja, AM Shah, S Yahya, *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science*, **2012**, 43A, 1382-1393
- [26] CA Loto, API Popoola, *International Journal of Electrochemical Science*, **2012**, 7, 2983-2996
- [27] HA Mohamed, *Journal of Applied Polymer Science*, **2012**, 125, 1790-1795
- [28] IB Obot, EE Ebenso ZM Gasem, *Int J Electrochem Sci* **2012**, 7, 1997-2008
- [29] AS Fouda, KM Elattar, *Journal of Materials Engineering and Performance*, **2012**, 21, 2354-2362
- [30] A Gulsen, *Research on Chemical Intermediates*, **2012**, 38, 1311-1321
- [31] LR Chauhan, G Gunasekaran, *Corros Sci*, **2007**, 49(3), 1143-1161
- [32] A Chetouani, B Hammouti, *Bull Electrochem* **2003**, 19, 23-25
- [33] A Bouyanzer, B Hammouti, *Resin & Pigment Technol* **2004**, 33(5), 287-392
- [34] M Benabdellah, M Benkaddour, B Hammouti, M Bendahhou, A Aouniti, *Appl Surf Sci* **2006**, 252(18), 6212-6217
- [35] A Zarrouk, H Zarrok, R Salghi, R Touir, B Hammouti, N Benchat, L L Afrine, H Hannache, M El Hezzat and M Bouachrine, *J Chem Pharm Res*, **2012**, 12(5), 1482-1491
- [36] M Dahmani, A Et-Touhami, SS Al-Deyab, B Hammouti, A Bouyanzer, *Int J Electrochem Sci*, **2010**, 5 (8), 1060-1069
- [37] L Afrine, A Zarrouk, H Zarrok, R Salghi, R Touir, B Hammouti, H Oudda, M Assouag, H Hannache, M El Harti and M Bouachrine, *J Chem Pharm Res*, **2013**, 12(5), 1474-1481
- [38] PC Okafor, ME Ikpi, IE Uwah, EE benso, UJ Ekpe, *Corros Sci* **2008**, 50, 2310-2317
- [39] AM Badiea, K N Mohana, *J Mater Eng Perfom*, **2009**, 18, 1264-1271
- [40] AY El-Etre, M Abdallah, Z E El-Tantawy, *Corros Sci* **2005**, 47, 385-395
- [41] M Kliškić, J Radošević, S Gudić, V Katalinić, *J Appl Electrochem* **2000**, 30, 823-830
- [42] M Lebrini, F Robert, C Roose, *Int J Electrochem Sci* **2010**, 5, 1698-1712
- [43] AS Verma, GN Mehta, *Bull Electrochem* **1999**, 15, 67-70
- [44] CA Loto, Loto, RT *Int J Electrochem Sci* **2011**, 6, 4900-4910
- [45] P C Okafor, EE Ebenso, JE Udofot, *Int J Electrochem Sci* **2010**, 5, 978-993
- [46] E E Oguzie, *Corros Sci* **2008**, 50, 2993-2998
- [47] H Hammouch, L Bennghmouch, A Srhiri, N Hajjaji *Cactusnet*, **2007**, (11), 57-61
- [48] C Belbachir, A Aouniti, M Khamri, A Chafi, B Hammouti, *J Chem Pharm Res*, **2013**, 12(5), 1307-1314
- [49] A Laqhaili, A Hakiki, M Mossaddak, M Boudalia, A Bellaouchou, A Guenbour, M El Morhit, B Hammouti, *J Chem Pharm Res*, **2013**, 12 (5), 1297-1306
- [50] H El Gharras, K Hnini, A Chtaini, A Hasib, A Jaouad *Natural Products, An Indian Journal*, **2009**, 5(4), 1-10
- [51] N Hajjaji, N Bettach, H Hammouch, A Srhiri, A Dermaj, and D Chebabe *OMPIC Morocco*, **2011**, Patent N°3069/10
- [52] H Hammouch, A Dermaj, N Hajjaji, N Bettach, A Srhiri, H Takenouti *Science Lib Editions Mersenne*, **2013**, 5, 130-201
- [53] D Bouknana, B Hammouti, A Bouyanzer, A Aouniti and M Sbaa, *J Chem Pharm Res*, **2012**, 12 (5), 1179-1194
- [54] D Bouzidi, A Chetouani, B Hammouti, S Kertit, M Taleb, SS Al-Deyab, *Int J Electrochem Sci*, **2012**, 7, 2334-2348