

## AQUEOUS EXTRACTS OF *OPUNTIA FICUS-INDICA* AS GREEN CORROSION INHIBITOR OF A283C CARBON STEEL IN 1N SULFURIC ACID SOLUTION

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**Abstract.** The effect of concentration and temperature were studied to measure the inhibiting capacity of extract *Opuntia ficus-indica* by using polarization and electrochemical impedance spectroscopy. The adsorption of the studied extract on carbon steel surface obeys the Langmuir adsorption isotherm.

**Keywords:** corrosion inhibition, polarization, adsorption, Nyquist diagram, green inhibitor.

### 1. Introduction

Carbon steel is one of the most important alloys, which is frequently used in a wide range of industrial applications. Corrosion problems arise due to the interaction of carbon steel with aqueous solutions, particularly during the pickling process, in which the alloy is brought into contact with highly concentrated acids [1, 2].

The use of inhibitors has been identified as a convenient and cheap means of combating steel corrosion. The inhibitors influence the kinetics of the electrochemical reactions which constitute the corrosion process, either by reducing the rate of metal dissolution in the corrosive medium and/or the cathodic reduction reaction. Corrosion inhibitors adsorb on the metal surface and thereby change the structure of electrical double layer [3]. Most of the efficient inhibitors used in industry are organic compounds that contain oxygen, sulfur, nitrogen atoms,  $\pi$ -bonds, and/or aromatic ring(s) in their molecules [4]. These electronegative atoms and functional groups have been reported to facilitate the adsorption of the inhibitors on metal surface [3, 5, 6].

This paper reports the effect of *Opuntia ficus-indica* extract as corrosion inhibitor for carbon steel in sulfuric acid solution.

### 2. Experimental

#### 2.1. Test Solutions

Working electrode is prepared from the carbon steel A283C. The chemical composition of the steel A283C is (wt %): carbon 0.18, S 0.05, P 0.06, Cu 0.20, the rest is iron [7]. The exposed area was mechanically abraded with 400, 500, 600, 1200 grade emery paper, washed with double distilled water, degreased with acetone and finally dried before each experiment.

A stock solution of 1N sulfuric acid with  $M = 98.8$  g/mol and density of  $1.83$  g/cm<sup>3</sup> was prepared from the concentrated acid solution (96 %), that was purchased from Merck and was used as received.

#### 2.2 Inhibitor Preparation

The extract of *Opuntia ficus-indica* (OFI) is obtained from the fig cladodes using vacuum filtration. Then we left the extract at the temperature of 277 K in the absence of light until the preparation of working solution.

#### 2.3. Electrochemical Measurements

The electrochemical measurements were carried out using a Volta lab PGZ 301 potentiostat and controlled by Tacussel corrosion analysis software model (Voltmaster 4 and EC-labdemo). The corrosion cell was a conventional three-electrode electrolysis cylindrical Pyrex glass cell. The working electrode had the form of a disc which was cut from a steel sheet. The surface area exposed to the corrosive solution was  $1$  cm<sup>2</sup>. A saturated calomel electrode SCE and a platinum electrode were used as reference and auxiliary electrodes, respectively. Electrochemical impedance spectroscopy (EIS) measurements were carried out after obtaining steady-state condition at the frequency ranged from 50 kHz to 100 mHz with a sine wave voltage (10 mV) peak to peak. The EIS data were given in Nyquist representation.

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Table 1

**Potentiodynamic polarization parameters for carbon steel in 1N H<sub>2</sub>SO<sub>4</sub> in the absence and the presence of OFI extract at 298 K**

OFI concentration, ppm	$E(i=0)$ , mV	$R_p$ , ohm·cm <sup>2</sup>	$i_{corr}$ , mA/cm <sup>2</sup>	$\beta_a$ , mV	$\beta_c$ , mV	$E$ , %
0	-454.7	16.63	1.8145	93.5	-136.9	–
10	-465.1	38.56	0.4352	45.0	-142.3	76.02
20	-456.1	49.86	0.3020	50.0	-142.3	83.35
30	-453.3	52.18	0.3002	41.3	-141.1	83.46
40	-453.1	73.02	0.2041	45.7	-171.4	88.75
50	-452.7	75.27	0.1918	37.5	-151.9	89.43

### 3. Results and Discussion

#### 3.1. Polarization Measurements

Fig. 1 represents potentiodynamic polarization curves for carbon steel in 1N H<sub>2</sub>SO<sub>4</sub> in the absence and the presence of various concentrations of OFI compounds. It can be seen that anodic and cathodic reactions of carbon steel with acid are inhibited in the presence of these molecules. Thus, addition of those inhibitor molecules reduces the carbon steel dissolution as retarding the hydrogen evolution reaction [7, 8]. Table 1 shows the electrochemical corrosion parameters as a corrosion potential ( $E_{corr}$ ), cathodic and anodic Tafel slopes ( $\beta_c$ ,  $\beta_a$ ), corrosion current density ( $i_{corr}$ ), obtained by extrapolation of the Tafel lines and the inhibition efficiency ( $E$  %), which was evaluated from Eq. (1):

$$E = \frac{1 - i_{corr}}{i_{corr}^0} \cdot 100 \quad (1)$$

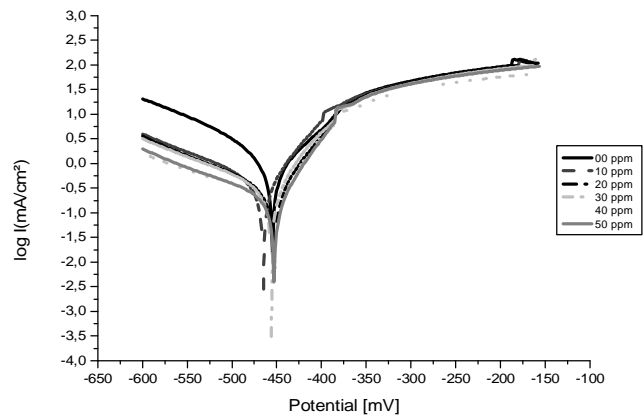
At both anodic and cathodic currents in the presence of these compounds the corrosion potentials shifted to the negative direction compared to the uninhibited carbon steel. Therefore, it could be concluded that this compound is of the mixed type. Corrosion inhibition efficiency increases as the inhibitor concentration increases [9]. OFI shows the maximum efficiency (89.43 %) at the concentration of 50 ppm.

#### 3.2. EIS Measurements

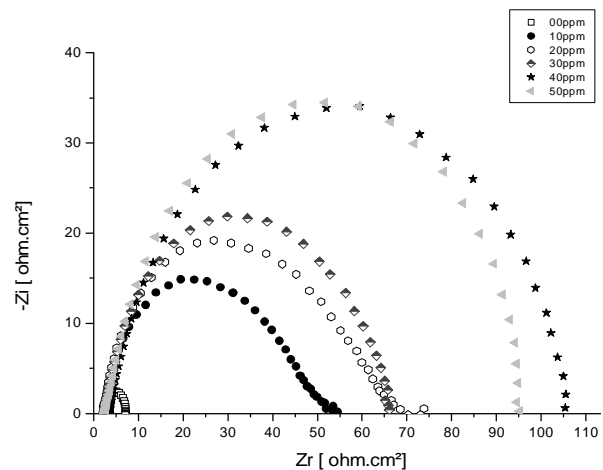
Fig. 2 shows the Nyquist diagrams of carbon steel in 1N H<sub>2</sub>SO<sub>4</sub> solution containing different concentrations of OFI at 298 K. All the impedance spectra exhibit one single semicircle.

The diameter increases with the increase of the OFI concentration. The semicircular appearance shows that the corrosion of carbon steel is controlled by the charge transfer and the presence of OFI does not change the mechanism of carbon steel dissolution [10, 11]. In addition, these Nyquist diagrams are not perfect semicircles. The deviation of semicircles from perfect circular shape is often referred to as the frequency dispersion of interfacial impedance [12]. This behavior is usually attributed to the inhomogeneity of the metal

surface arising from surface roughness or interfacial phenomena [12, 13], which is typical of solid metal electrodes. Generally, when a non-ideal frequency response is present, it is commonly accepted to employ the distributed circuit elements in the equivalent circuit (Fig. 3.) What is most widely used is the constant phase element (CPE), which has a non-integer power dependence on the frequency [5, 12-14].



**Fig. 1.** Polarization curves of A283C steel in 1N H<sub>2</sub>SO<sub>4</sub> in the absence and presence of OFI extract with different concentrations at 298 K

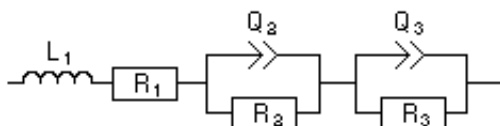


**Fig. 2.** Nyquist diagrams of carbon steel with different concentrations of OFI at 298 K

Table 2

**Values associated with the impedance parameters on the corrosion of A283C steel in the mild-H<sub>2</sub>SO<sub>4</sub> in the presence and absence of the inhibitor**

OFI concentration, ppm	$R_1$ , ohm·cm <sup>2</sup>	$R_3$ , ohm·cm <sup>2</sup>	$C_{dl}$ , μF/cm <sup>2</sup>	$E_Z$ , %
0	1.989	5.254	1211	
10	2.034	42.09	189.0	84.39
20	1.914	54.44	184.7	84.75
30	2.289	59.47	169.1	86.04
40	3.050	103.8	153.1	87.36
50	2.543	92.26	137.9	88.61


**Fig. 3.** Electrical equivalent circuit used to fit the experimental impedance data

In this equivalent circuit  $R_1$  and  $L_1$  are the resistance and the inductor of the solution.  $Q_2$  and  $R_2$  are the CPE and the resistance of the protective layer,  $Q_3$  and  $R_3$  correspond to the double layer.

The impedance of CPE is defined according to Eq. (2):

$$Z(f) = L_1 i 2\pi f + R_1 + \frac{R_2}{R_2 Q_2 (i 2\pi f)^{a_2} + 1} + \frac{R_3}{R_3 Q_3 (i 2\pi f)^{a_3} + 1} \quad (2)$$

As can be seen from Table 2, the  $C_{dl}$  values decrease with the increase of OFI concentration, which suggests that OFI functions by adsorption on the carbon steel surface. It is inferred that the OFI molecules gradually replace the water molecules by adsorption at the metal/solution interface, which leads to the formation of a protective film on the carbon steel surface and thus decreases the extent of the dissolution reaction [15, 16]. Moreover, the increase of OFI concentration leads to the increase of  $R_3$  and  $E_Z$  values. The corrosion inhibition efficiency reaches more than 88 % in the presence of 50 ppm OFI. The values of percentage inhibition efficiency  $E_Z$  (%) were calculated from the values of  $C_{dl}$  according to Eq. (3) [13]:

$$E_Z = \left[ 1 - \left( \frac{C'_{dl}}{C_{dl}} \right) \right] \cdot 100 \quad (3)$$

where  $C'_{dl}$  and  $C_{dl}$  are the capacity double layer values with and without inhibitor, respectively.

### 3.3. Effect of Temperature

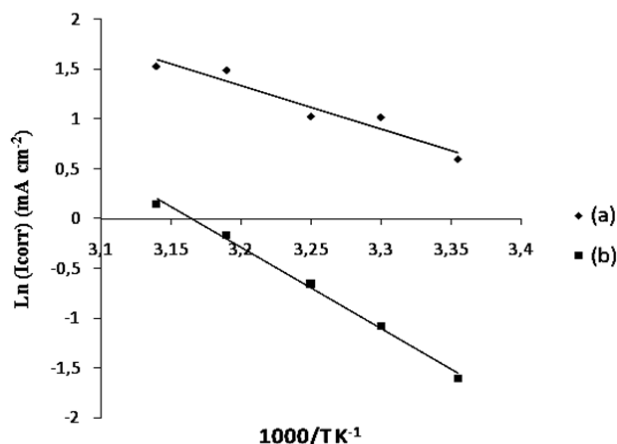
The effect of temperature on the various corrosion parameters  $E_{corr}$ ,  $i_{corr}$ ,  $q$  (surface coverage), and  $E$  was

studied in 1N H<sub>2</sub>SO<sub>4</sub> within the temperature range of 298–318 K in the absence and the presence of 50 ppm of OFI. The activation parameters were calculated from the Arrhenius-type plot according to Eq. (4) [3, 16]:

$$i_{corr} = K \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where  $E_a$  is the apparent activation corrosion energy, kJ/mol;  $R$  is the universal gas constant, J·mol<sup>-1</sup>·K<sup>-1</sup> and  $K$  is the Arrhenius pre-exponential constant.

Arrhenius plots for the corrosion density of carbon steel in the case of OFI are given in Fig. 4. Values of apparent activation energy  $E_a$  of corrosion for carbon steel in 1.0N H<sub>2</sub>SO<sub>4</sub> in the absence and presence of OFI were determined from the slope of  $\ln(i_{corr})$  versus  $1/T$  plots and shown in Table 3.


**Fig. 4.** Plot of  $\ln(i_{corr})$  vs.  $1000/T$  for A283C carbon steel in 1N H<sub>2</sub>SO<sub>4</sub> without inhibitor (a) and in the presence of 50 ppm of OFI (b)

#### 3.3.1. Activation parameters and adsorption isotherm

An alternative formula of the Arrhenius equation is the transition state equation [2, 16, 17]:

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (5)$$

where  $h$  is Plank's constant, J-s;  $N$  is the Avogadro's number,  $\text{mol}^{-1}$ ;  $\Delta S^*$  is the entropy of activation, J/mol-K;  $\Delta H^*$  is the enthalpy of activation, kJ/mol

A plot of  $\ln(i_{corr}/T)$  versus  $1/T$  gave a straight line (Fig. 5), with a slope of  $(-\Delta H^*/2.303R)$  and an intercept of  $[\log(R/Nh) + (\Delta S^*/2.303R)]$ , from which the values of  $\Delta S^*$  and  $\Delta H^*$  were calculated and listed in Table 3 [15, 18].

According to the literature, higher value of  $E_a$  was considered as physical adsorption that occurred at the first stage. Because the electrochemical corrosion is relevant to heterogeneous reactions, the pre-exponential factor  $A$  in the Arrhenius equation is related to the number of active centers. There are two possibilities about these active centers with different  $E_a$  on the metal surface: (i) the activation energy in the presence of inhibitors is lower than that of pure acidic medium, namely  $E_a(\text{-inh}) < E_a(\text{H}_2\text{SO}_4)$ , which suggests that a smaller number of more active sites remain uncovered in the corrosion process; (ii) the activation energy in the presence of inhibitor is higher than that of pure acidic medium,  $E_a(\text{inh}) > E_a(\text{H}_2\text{SO}_4)$ , which represents the inhibitor adsorbed on most active adsorption sites (having the lowest energy) and the corrosion takes place chiefly on the active sites (having higher energy) [3, 17].

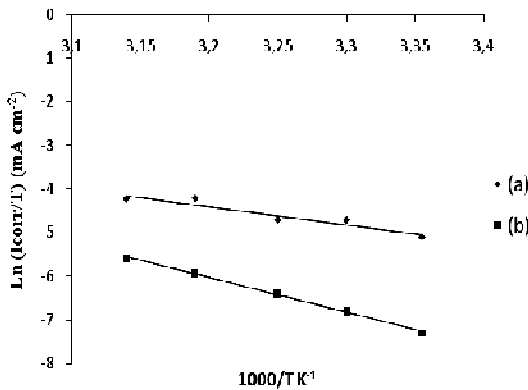


Fig. 5.  $\ln(i_{corr}/T)$  vs.  $1000/T$  for A283C carbon steel in 1N  $\text{H}_2\text{SO}_4$  without inhibitor (a) and in the presence of 50 ppm of OFI (b)

Table 3

The thermodynamic activation parameters in the presence of the inhibitor OFI

Inhibitor	$E_a$ , kJ/mol	$\Delta H_a$ , kJ/mol	$\Delta S_a$ , J/mol K	$\Delta G_{ads}^0$ , kJ/mol
Blank	83.717	34.65	-122.970	-
OFI	155.968	65.65	-37.350	-7.36

The data in Table 3 specifically indicate that the value of  $E_a$  in the presence of OFI is greater than that in the absence of OFI. Thus, it is clear that the adsorption of OFI on carbon steel surface blocks the active sites from

acid solution and consequently increases the apparent activation energy. Then, it can be suggested that the OFI adsorb by physisorption mechanism on the metallic surface [8, 16].

The positive sign of the enthalpy ( $\Delta H_a$ ) reflects the endothermic nature of the steel dissolution process. The negative value of  $\Delta S^*$  for the inhibitor indicates that activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder takes place during the course of transition from reactant to the activated complex (Fig. 5) [11, 17, 19].

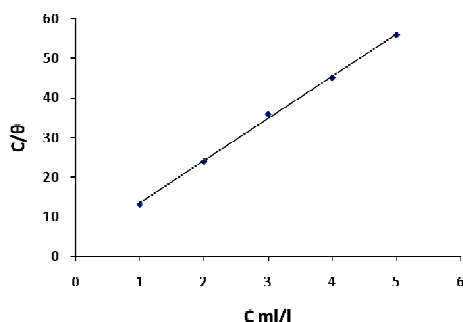
3.3.2. Adsorption isotherm and standard adsorption free energy

It is essential to know the mode of adsorption and the adsorption isotherm, which can give valuable information on the interaction of inhibitor and metal surface [19, 20]. Values of surface coverage ( $\theta$ ) corresponding to different concentrations of OFI calculated using the results at 298 K after 30 min of immersion were used to determine which isotherm best described the adsorption process.

The results obtained for the investigated inhibitor in 1N  $\text{H}_2\text{SO}_4$  solution were tested with adsorption isotherms. However, the best fit to the experimental data was obtained with the Langmuir adsorption isotherm equation as follows [21, 22]:

$$\frac{C_{inh}}{q} = \frac{1}{K_{ads}} + C_{inh} \quad (6)$$

The primary step in the action of inhibitors in acid solution is generally agreed to be adsorption on the metal surface [17, 18, 20]. 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 occurred normally on the inhibitor free area. Accordingly, the inhibition efficiency is directly proportional to the fraction of the surface covered by adsorbed molecules ( $\theta$ ), which was calculated in this case using the equation  $\theta = E/100$ . The surface coverage data are very useful while discussing the adsorption characteristics [18-20]. 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 dependence of the fraction of the surface covered  $\theta$  on the concentration  $C$  of the inhibitor was tested graphically by fitting it to Langmuir's isotherm, which assume that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species [16, 17]. Fig. 6 shows the linear plots for  $C/\theta$  versus  $C$  with  $R^2 = 0.9986$ , suggesting that the adsorption obeys the Langmuir's isotherm.



**Fig. 6.** Plot of  $C_{inh}/\theta$  vs.  $C_{inh}$  for carbon steel in the presence of different concentrations of inhibitor

### 3.4. Thermodynamic Parameters

To calculate the adsorption constant  $K_{ads}$  and the adsorption energy  $\Delta G_{ads}^0$  we must use the following equation:

$$\Delta G_{ads}^* = -RT \ln(55.5 K_{ads}). \quad (7)$$

The  $K_{ads}$  and  $\Delta G_{ads}^0$  values calculated for the model Langmuir are shown in Table 3.

Generally, values of  $\Delta G_{ads}^0$  around  $-20 \text{ kJ}\cdot\text{mol}^{-1}$  or lower are consistent with the electrostatic interaction between charged molecules and the charged metal surface (physical sorption), those around  $-40 \text{ kJ}\cdot\text{mol}^{-1}$  or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of metal bond (chemical sorption) [18]. Based on the literature [3, 17, 22], the calculated  $\Delta G_{ads}^0$  value in this work indicates that the adsorption mechanism of OFI on carbon steel is a physical sorption; an adsorptive film with an electrostatic character is formed. However, some researchers have reported that adsorption of inhibitor molecules obeys a comprehensive adsorption (physical and chemical adsorption) for the same values [22, 23].

### 4. Conclusions

Results obtained from electrochemical impedance spectroscopy and potentiodynamic polarization data showed that the extract of OFI can act as efficient corrosion inhibitor for carbon steel in sulfuric acid solution with maximum inhibition efficiency of 88 % at 298 K. Adsorption of inhibitor follows Langmuir adsorption isotherm by forming a monolayer on metal surface. This result was confirmed by application of adsorption model. Values of heat of adsorption were low indicating a physical adsorption on metal surface.

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### ВОДНІ ЕКСТРАКТИ ОПУНЦІЇ ІНДІЙСЬКОЇ (*OPUNTIA FICUS INDICA*) ЯК ЕКОЛОГІЧНО-БЕЗПЕЧНОГО ІНГІБІТОРА КОРОЗІЇ ВУГЛЕЦЕВОЇ СТАЛІ А283С В 1N СУЛЬФАТНІЙ КИСЛОТІ

**Анотація.** З використанням поляризаційної та електрохімічної імпедансної спектроскопії вивчено вплив концентрації та температури на інгібуючу здатність екстракту опунції індійської. Встановлено, що адсорбція досліджуваного екстракту на поверхні вуглецевої сталі відповідає ізотермі адсорбції Ленгмюра.

**Ключові слова:** інгібування корозії, поляризація, адсорбція, діаграма Найквіста, екологічно-безпечний інгібітор.