December 2009 Volume 5 Issue 4

Trade Science Inc.

Natural Products

An Indian Journal

Full Paper

NPAIJ, 5(4), 2009 [175-183]

Natural corrosion inhibition of stainless steel in phosphoric medium by betacyanin and betaxanthin pigments extracted from moroccan prickly pear juices

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Received: 21st September, 2009 ; Accepted: 1st October, 2009

ABSTRACT

The inhibitive action of natural pigments (Red and Yellow) extracted from prickly pear fruits (*Opuntia ficus-indica*) towards corrosion of stainless steel in phosphoric acid was investigated using, electrochemical polarisation and electrochemical impedance spectroscopy (EIS) methods. It was found that the presence of natural pigments reduce the corrosion rate of the tested metal especially in addition of the red pigments (97%). The inhibition efficiency increases as the pigment concentration of extracts increased. It was also found that the pigments tested act as mixed inhibitors. The inhibitive action of the extracts is discussed in term of adsorption and that such adsorption follows Langmuir adsorption isotherm. The calculated values of the free energy of adsorption indicated that the adsorption process is spontaneous.

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KEYWORDS

Stainless steel;
Phosphoric acid;
Corrosion inhibitors;
Natural products;
Betalains;
Prickly pear;
Juice;
Opuntia ficus-indica.

INTRODUCTION

Phosphoric acid is a major chemical product which has many important uses, especially in the production of fertilizers. Most of the acid is produced from phosphate rocks and acid solution of H_2SO_4 or HCl. Crude H_3PO_4 from the attack stage is filtered and concentrated in evaporation units[1]. There is a great need to protect steel material used in phosphoric acid industry from corrosion.

Among the several methods of corrosion control and prevention, the use of corrosion inhibitors[2-7] is very popular. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency. But, unfortunately most of these compounds are not only expensive but also toxic to living beings. It is needless to point out the importance of cheap, safe inhibitors of corrosion.

Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. There

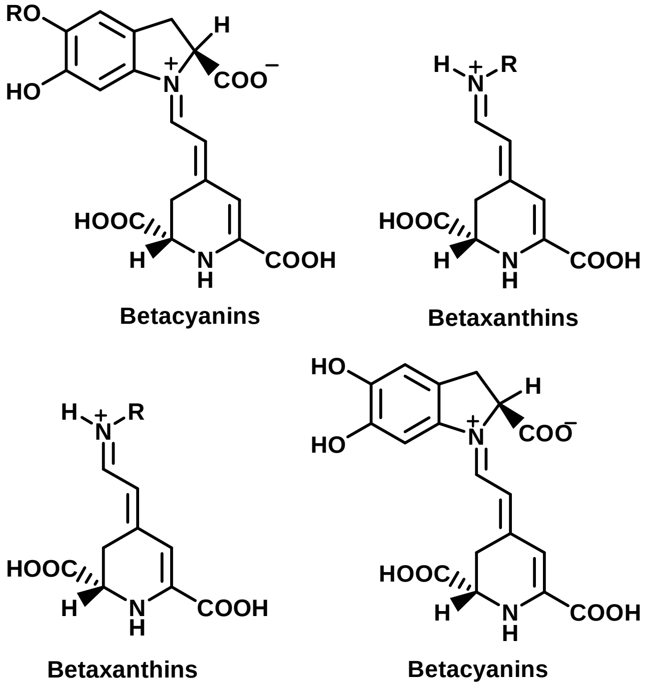

Figure 1 : Chemical structure of betacyanins and betaxanthins

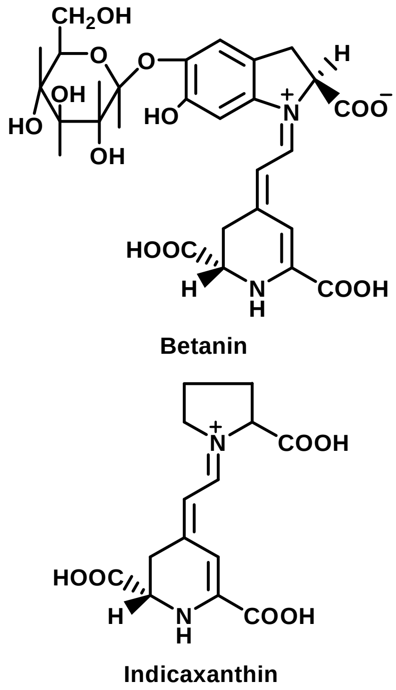

Figure 2 : Chemical structure of betanin and betaxanthin

are rich sources of ingredients which have very high inhibition efficiency. Many works were performed to examine extracts from natural substances[8-25]. These organic compounds are either synthesised or extracted from aromatic herbs, spices and medical plants. Naturally occurring antioxidants are cheap and environmental safe substances. Their use as corrosion inhibitor has been preferred. One of these sources is *Opuntia ficus-indica* which contains a particular class of water-soluble pigments 'Betalains'. Betalains are a class of yellow (betaxanthins) or violet (betacyanins) vacuolar water-soluble chromo-alkaloid pigments accumulating in flowers, fruit and sometimes in vegetative tissues of plants from the Caryophyllales order. The chemical structure of these pigments derives from betalamic acid and, depending on the components bonded to the main structure, betacyanins or betaxanthins arise, the former when the group is 3,4-dihydroxyphenylalanine (DOPA), which may or may not be glycosylated, and the latter if the conjugation partners are amino acids or derived amines (Figure 1). Analyses of prickly pear fruits pigment extracts have indicated the presence of purple-red betanin and yellow-orange indicaxanthin, which changes in the proportion confer the different colors to the fruits[26-29] (Figure 2). Beside to their coloring property, betanin and indicaxanthin have, themselves, antioxidant activities[30,31]. In one hand it was reported that *Opuntia* extract inhibits aluminium corrosion in HCl solution with inhibition efficiency about 96%[32], and in the other hand, little work have been done on the inhibition of steel in H_3PO_4 solution[33-38]. These reasons has incited us to examine plant extracts as corrosion inhibitor of steel in 30% H_3PO_4[39-41].

This work is devoted to examine the betacyanin and betaxanthin extracted from Moroccan cactus pear juice leaves as an inhibitor for corrosion of stainless steel in 30% H_3PO_4 solution. UV Spectrophotometry, Electrochemical polarisation and EIS measurement were used in this study to reach this objective.

EXPERIMENTAL

Materials

316 L steel was used as working electrode in the present study. The chemical composition of this steel is:

0.02% C, 0.50% Si, 1.71% Mn, 16.20%Cr, 11.00% Ni, 2.18% Mo, 0.35% Cu, 0.07% N, 0.03% P, 0.023% S, and the remainder is iron.

The aggressive solution (30% H_3PO_4) is prepared by dilution of analytical grade 85% H_3PO_4 with double distilled water.

Mature Moroccan Prickly pears (*Opuntia ficus-indica*), of yellow and red color, were used in this investigation. The fruit samples were harvested in August from Skhour Rehamena, washed in tap water, peeled and stored at -20°C. The pulp and juice were separated from seeds by filtration (Whatman, NJ, USA). The juices were kept at -20°C until taken for analysis. In the following, we will refer to filtered juices as juice. The filtrates were subjected to the pigment extraction. The betacyanin and/or betaxantin extracts were dissolved in 30% H_3PO_4 solution.

Pigments analysis and quantification

The pigments were extracted from the filtered juice. The juice was homogenized in methanol (analytical grad, ALDRICH, Deisenhofen, Germany) (1:5 W/V) and magnetically stirred for 1 min. The homogenate was filtered through a 0.45μm nylon filter (WHATMAN, USA). UV-Visible absorbance spectra of the extracts were recorded using a double-beam spectrophotometer (Shimadzu UV Visible 160A°, Tokyo, Japan) equipped with one-cm optical-path quartz cells.

Due to the lack of commercially available reference substances and because of the lability of the compounds, betalains are usually quantified spectrophotometrically using molar extinction coefficients of betanin or indicaxanthin, representative for betacyanins and betaxanthins, respectively[42,43]. Indicaxanthin and betanin concentrations were estimated using the extinction coefficients calculated by Girod and Zryd (1991) and Wyler *et al*, (1959), respectively[44,45].

Electrochemical measurements

Electrochemical measurements are carried out in a conventional three-electrode electrolysis cylindrical pyrex glass cell. The temperature is controlled at 288±1 K. The working electrode (WE) in form of rectangular cut from steel, has a geometric area of 1cm^2. A saturated calomel electrode (SCE) and platinum electrode are used as reference and auxiliary electrode, respectively. Before each experiment, the working electrode was polished mechanically using successive grades of emery papers up 2000 grit, rubbed with a smooth polishing cloth, then washed with double distilled water and transferred quickly to electrochemical cell.

The impedance measurement and polarisation measurements were performed using the voltalb 10 PGZ 100 piloted by master 4 software for calculation of corrosion parameters (corrosion current density, corrosion potential, resistance of polarization and Tafel constants). The potentials were measured against and referred to the saturated calomel electrode (SCE). All potentiodynamic polarization measurements were carried out using a scan rate of 10 mVs^{-1}. In the case of polarization method the relation (1) determines the inhibition efficiency (E%)

$$\mathbf{EI} = \left(\frac{\mathbf{1 - I_{corr}}}{\mathbf{I^0_{corr}}}\right) \mathbf{X\,100} \qquad \mathbf{(1)}$$

I°_{corr} and I_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic and anodic Tafel lines to corrosion potential.

Electrochemical impedance spectroscopy (EIS) was carried at E_{corr} after immersion in solution. After the determination of steady-state current at a given potential, sine wave voltage (10mV) peak to peak, at frequencies between 100kHz and 10mHz were superimposed in the rest potential. The computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. The impedance diagrams are given in the Nyquist representation.

The inhibition efficiency, got from the charge transfer resistance, is calculated from the following equation[46]:

$$\mathbf{Inh_{Rct}\,\%} = \left(\frac{\mathbf{R^{-1}_{ct_0} - R^{-1}_{ct}}}{\mathbf{R^{-1}_{ct_0}}}\right) \mathbf{X\,100} \qquad \mathbf{(2)}$$

Where R_{ct0} and $R_{ct,}$ are respectively, the charge-transfer resistance values of sainless steel with and without inhibitor.

RESULTS AND DISCUSSION

Betalain pigment quantification

Figures 3 and 4 show the UV-Visible absorption spectra of the methanolic extracts of the yellow and reddish prickly pear fruits (Figure 1). The UV-Visible absorption spectrum of pigments extracted from yellow fruits shows one absorption maximum at 479nm, which corresponds to indicaxanthin[47,27,31]. The absence of absorbance peak at 536nm in the visible part of the spectrum indicated that betacyanins are found in very low levels in juices derived from yellow fruits (TABLE 1).

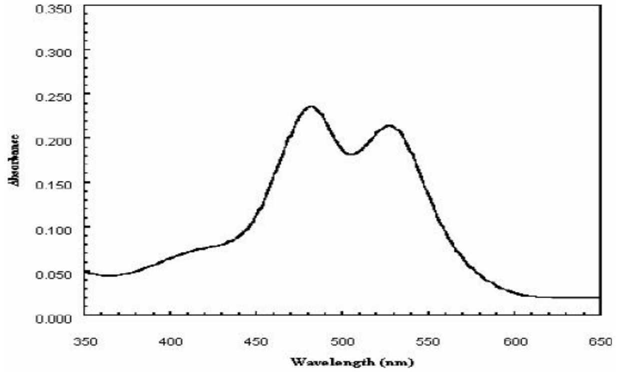

Figure 4 : Room temperature UV-Visible absorbance spectrum of the methanolic extract of the reddish cactus pear juice

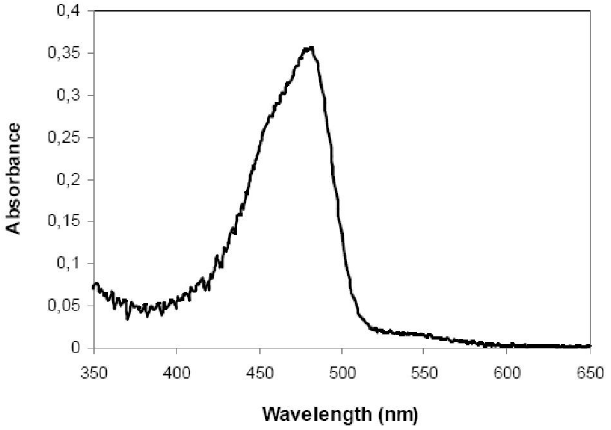

Figure 3 : Room temperature UV-Visible absorbance spectrum of the methanolic extract of the yellow cactus pear juice

TABLE 1 : Amounts of betaxanthins and betacyanins (mg per kg of juice) in yellow juices of cactus pear cultivated at different regions

Origin	Betaxanthin	Betacyanin	References
Morocco	76.3	Traces	This study
Italy	48.3	1.3	[43:Stintzing & Schieber, 2003]
Italy	84.2	10.4	[31:Butera & al. 2002]
Spain	250.0	-	[27:Fernandez-Lopez & Almela, 2001]

TABLE 2 : Amounts of betaxanthins and betacyanins (mg per kg of juice) in reddish cactus pear cultivated at different regions

Origin	Betacyanins	Betaxanthins	References
Morocco	13,23	11,08	This study
Italy	51,20	26,10	[31:Butera & *al*. 2002]
Italy	73,90	36,40	[43:Stintzing & *al*. 2003]
Italy	140,00	400,00	[26:Forni & *al*. 1992]
Spain	143,00–801,00	-	[29:Castellar & *al*. 2003]
Spain	190,00	300,00	[27:Fernandez-Lopez & Almela. 2001]

The UV-Visible absorption spectrum of reddish fruits is more complex and presents two bands. The maxima reflect the presence of indicaxanthin and betanin absorbing at 484nm and 532 nm, respectively (Figure 2)[26,27,29].

On average, the amount of betaxanthins detected in yellow fruits is 76.38mg of indicaxanthin per 1kg of juice (TABLE 1). While, in reddish fruits the amounts detected corresponding respectively to betaxanthin and betacyanin are 11.08mg of indicaxanthin and 13.23mg of betanin per 1Kg of juice (TABLE 2).

Pigment quantification indicated that the amount of indicaxanthin in yellow fruits is in the same order as in plants grown in Italy, but not in Spain (TABLE 1)[27,31,43].

While the amounts of betaxanthins and betacyanins detected in reddish fruits are very low than those reported for Italian and Spanish fruits (TABLE 2)[31,43,26,29].

At present, no explanation for these differences is known but they may have resulted from differences in cactus ecotypes, physiology, seasons or extraction procedures.

Open-circuit potential measurements

The open circuit potentials of stainless steel in the absence and presence of pigment extracted from prickly pear fruits (*Opuntia ficus-indica*), grown in Morocco were traced over 35 min from the electrode immersion in the 30% H_3PO_4 solution. The results are presented in (Figure 5). The steady state potential tends to decrease and stabilize after 21 min. The presence of pigment extracts in acidic solution shifted the steady-state potential towards more positive values. The potential shift can be attributed to the adsorption of molecules contained in extracts of cactus pear juice on the active sites and/or the deposition of corrosion product on the electrode surface[40,41].

Potentiodynamic study

The polarisation curves of steel in 30% H_3PO_4 devoid of and containing 0.2mL/L extracted pigments at 293°K are presented in Figure 6. In presence of these extracted pigments the cathodic current potential curves give rise to parallel Tafel lines indicating that the hydrogen evolution reaction is activation controlled and the presence of compounds tested does not modify the mechanism of this reaction. In the anodic domain, the addition of these pigment extracts decreases the current densities in large domain of potential; this decrease is very important in presence of red pigment in both anodic and cathodic domain. The collected parameters deduced from the polarisation curves, such as the corrosion potential (E_{corr}), corrosion current (I_{corr}), cathodic and anodic Tafel slopes (Bc, Ba) and percentage inhibition are shown in TABLE 3. The inhibition efficiency (E%) is determined by using the equation (1). The inhibition efficiency (E%) of red pigment is higher than the yellow, this behaviour can be attributed to the presence of more electron donor groups in the molecular structure of red pigments. This propriety favours the adsorption of red pigments[19,21,41].

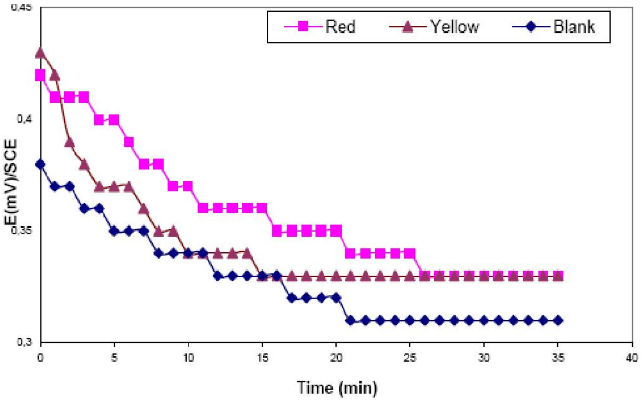

Figure 5 : Variation of the open circuit potential with time for stainless steel of the electrode immersion in phosphoric acid with and without pigment extracts

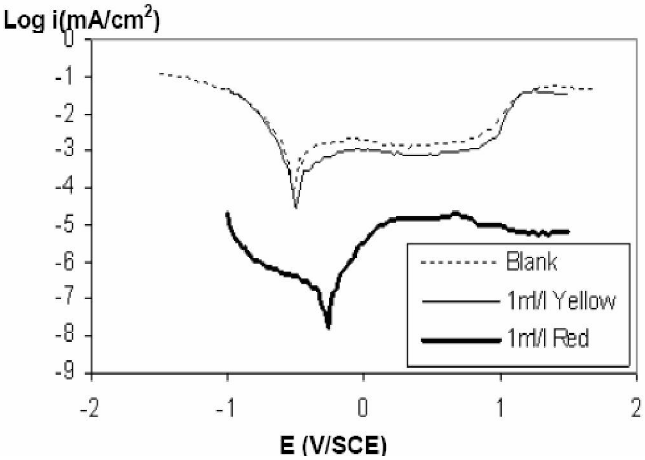

Figure 6 : Potentiodynamic polarization curves of 316L Stainless steel after 30 min of the electrode immersion in 30% H_3PO_4 solutions in absence and in the presence of pigment extracts at 293 K

TABLE 3 : Electrochemical parameters for stainless steel in phosphoric acid in presence of 0.2mL/L yellow and red pigments extracted from Moroccan yellow and reddish cactus pear juices

[mL/L]	E(i=0) mV/SCE	RP (Ω.cm^2)	j_{corr} (mA/ cm^2)	b_a (mV/SCE) /dec	b_c (mV/SCE) /dec	EI (%)
Blank	-505	153	0,31	303	-182	-
Yellow pigment (0,2mL/L)	-501	202	0,11	286	-167	63
Red pigment (0.2mL/L)	-483	209	0,02	195	-280	92

EIS measurements

The results of the potentiodynamic polarization experiments were confirmed by impedance measurements, since the electrochemical impedance spectroscopy (EIS), is a powerful technique in studying corrosion mechanisms and adsorption phenomena[48]. The experimental impedance results are simulated to pure electronic models that can verify or role out mechanistic models and enables the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system under investigation[49,50,51].

The effect of the presence of the pigment extract on the corrosions behaviour of steel electrode in phosphoric acidic solutions was investigated. The Nyquist plots for steel electrode in absence and then in the presence of extracts in phosphoric solutions are presented in Figure 7. The locus of Nyquist plots is regarded as one part of semi circle in absence and in presence of red pigments but in presence of yellow pigments the Nyquist plots are not perfect semicircles. This feature had been attributed to frequency dispersion

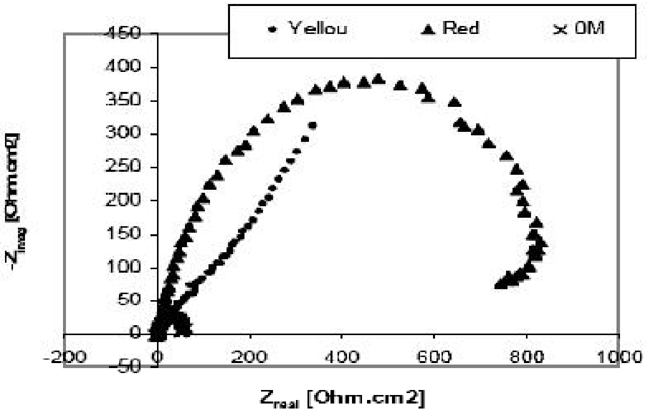

Figure 7 : Nyquist plots for 316L Stainless steel after 30 min of the electrode immersion in 30%H_3PO_4 solutions in absence and in the presence of 0.2ml/l pigments extract at 293 K

of interfacial impedance[52]; this anomalous phenomenon may be attributed to the inhomogeneity of electrode surface arising from surface roughness or interfacial phenomena[53,54].

The inhibition efficiency, as determined from EIS methods, was found to vary in order yellow pigment<red pigment which is in a good agreement with the result obtained by potentiodynamic measurement. This result is mainly due to the polarity of molecule. It is well known that different substituents on the organic molecule polarize the functional group in a different manner[55]. Impedance parameters derived from this investigation are given in TABLE 4. As we notice, in the presence of pigment extracts, the R_{tc} values increased, but C_{dl} values tended to decrease. The decrease in C_{dl} values Suggested that red pigments, function by adsorption of red pigments at the metal-solution interface[56] and decrease in local dielectric constant and /or an increase in the thickness of the electrical double layer.

TABLE 4 : Impedance parameters for stainless steel in phosphoric acid in presence of yellow and red pigments extracted from Moroccan cactus

Compound	R_1(Ω.cm^2)	R_2(Ω.cm^2)	C(μF.cm^{-2})	E%
Blank	3,23	60	720	_
yellow pigments (0,2 mL/L)	1,4	400	130	79
red pigments (0,2 mL/L)	1,03	986	114	93

Detailed study of red pigments polarisations curves

The cathodic and anodic polarization curves of 316 L stainless steel in solutions of 30% H_3PO_4 in presence of different concentrations of extracted red pigments are represented in Figure 8. Inspection of the figure reveals that the polarization curves are shifted toward more positive potentials and less current density upon addition of pigment extract. This result confirms the inhibitive action of the pigment extract toward acid corrosion 316 L steel. The corrosion parameters of steel in solutions were calculated from polarization curves and presented in TABLE 5. Inspection of data of the TABLE revealed that the corrosion potential shifts to more positive values with increased concentrations of pigment extract. Moreover, the corrosion current density decreases markedly on addition of the extract. The magnitude of this decrement increases as the concentration of the extract is increased. Therefore, the inhibition efficiency increases with increasing extract concentration. Further inspection of the TABLE reveals that both the anodic and cathodic Tafel constants change with increasing extract concentration. This result suggests that the presence of the extract affects the anodic dissolution of steel as well as the cathodic reduction of hydrogen ions. Therefore, it could be concluded that the molecules of extract absorb onto both anodic and cathodic sites of the steel surface. This behaviour indicates that the extract acts as a mixed inhibitor.

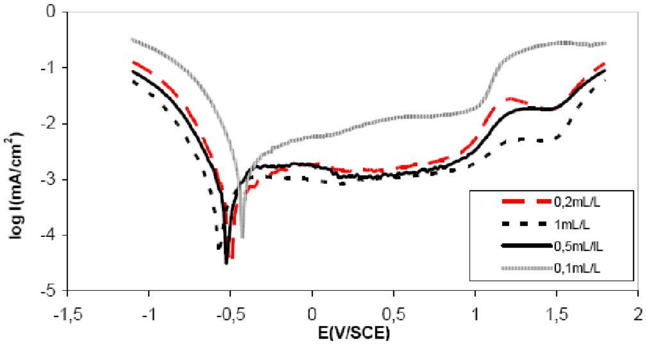

Figure 8 : Potentiodynamic polarization curves of 316L Stainless steel after 30 min of the electrode immersion in 30%H_3PO_4 solutions in absence and in the presence of red pigment extract at different concentrations at 25°C

TABLE 5 : Electrochemical parameters for stainless steel type 316 in phosphoric acid in presence of different concentrations of red pigments

[mL/L]	E(i=0) mV	Rp (Ω.cm^2)	j_{corr} (μA/ cm^2)	b_a (mV/dec)/SCE	b_c (mV/dec)/SCE	E(%)
Blank	-505	153	310	303	-182	-
0,1	-496	195	110	286	-172	65
0.2	-483	209	23	195	-280	92
0.5	-473	226	21	156	-265	93
1.0	-341	426	8	153	-242	97

The adsorption isotherm

To obtain more informations about the interaction between betacyanin and betaxantin molecules contained in pigment extracts and the electrode surface, different adsorption isotherms were investigated. The degree of surface coverage, θ, at different concentrations of red pigments in phosphoric acid solutions was calculated from the corresponding electrochemical polarization measurements according to[61]:

$$\theta = \frac{I_{corr} - I_{corr_{inh}}}{I_{corr}} \qquad (6)$$

The obtained values of θ were fitted to different isotherms including Langmuir, Frumkin, and Temkin etc. The Langmuir isotherm, Eq. (7), was verified in the case of red pigment extract, which is based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites being occupied or not[62].

$$\mathbf{KC} = \frac{\theta}{\mathbf{1}-\boldsymbol{\theta}} \tag{7}$$

where C is the concentration of the inhibitor, θ, the fractional surface coverage and K is the adsorption equilibrium constant. The value of K is related to the free energy of adsorption ΔGads as[62,63]:

$$\mathbf{K} = \frac{\mathbf{1}}{\mathbf{C}_{\mathbf{solvent}} \times \mathbf{exp}(\frac{-\Delta \mathbf{G}_{\mathbf{ads}}}{\mathbf{RT}})} \tag{8}$$

Where Csolvent represents the molar concentration of the solvent which is 55.5 mol dm^{-3} in the case of water, R the universal gas constant and T is the temperature. The Langmuir adsorption isotherm can be rearranged to obtain the following mathematical formulation:

$$\frac{\mathbf{C}}{\boldsymbol{\theta}} = \frac{\mathbf{1}}{\mathbf{K}+\mathbf{C}} \tag{9}$$

A linear relationship can be obtained on plotting C/θ as a function of C, with a slope of unity, and the value of the intercept is the reciprocal of K. The results of the adsorption of pigment extract in 30% H_3PO_4 solutions are presented in Figure 9, the expected linear relationship is obtained and the value of the free energy of adsorption of pigment extract on steel, G_{ads}, was calculated to be -29KJ/mol. The negative sign indicates that the adsorption of extract components onto the steel surface is spontaneous process[57,58,59]. It is well known that values of G_{ads} on the order of -20kJ/mol or lower indicate a physical adsorption, while value of -40kJ/mol is usually adopted as a threshold value between chemi- and physisorption[60]. The calculated value for the adsorption of extract on Steel electrode indicates that adsorption is of a physical nature, and there is no chemical interaction between the inhibitor molecule and the metal surface.

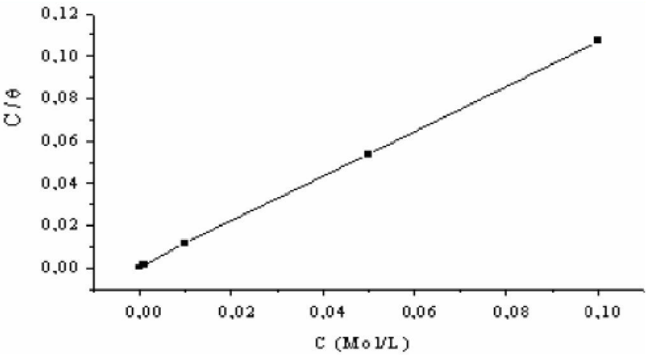

Figure 9 : Adsorption isotherm for the adsorption of red pigment extract on stainless steel in 30%H_3PO_4 solutions at 298K

The electrochemical impedance measurements

Similar Nyquist are obtained for steel in absence and presence of different concentrations of red pigment extract. Generally the Nyquist plots show a single loop frequency, which indicates the presence of one time constant representing the electrode process. The values of the corrosion resistance, R_{corr}, and the thickness of the passive film, $1/C_{dl}$[54], increase in the presence of the pigment extract, which can be attributed to the adsorption of the extract molecules on the electrode surface. The increase of R_{corr} and $1/C_{dl}$ is remarkable in height pigment concentration, the highest value of $1/C_{dl}$ indicating a

TABLE 6 : Impedance parameters for stainless steel in phosphoric acid in presence of different concentrations of red pigments

Volume d'extrait (mL/L)	R_1 (Ωcm^2)	R_2 (Ωcm^2)	C_{dl}(μF cm^{-2})	$1/C_{dl}$ (μF $cm^{-2})^{-1}$	θ
Blank	3,2	60	720	0,001	-
0.1	4,4	416	245	0,004	0,85
0,2	1,03	986	130	0,007	0,93
0.5	4,6	1002	114	0,008	0,94
1.0	2,8	1300	92	0,010	0,95

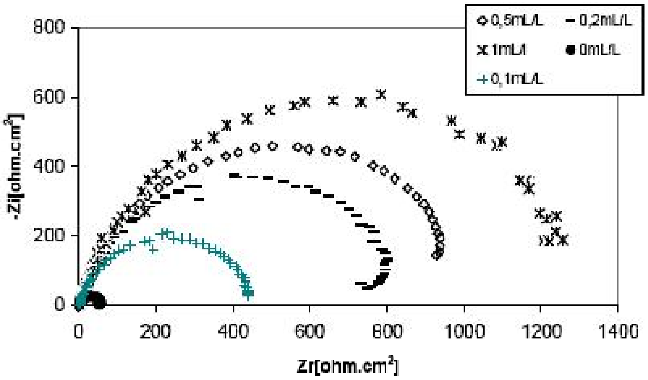

Figure 10 : Nyquist plots for 316L Stainless steel after 30 min of the electrode immersion in 30% H_3PO_4 solutions in absence and in the presence of red pigment extract at different concentration at 298K

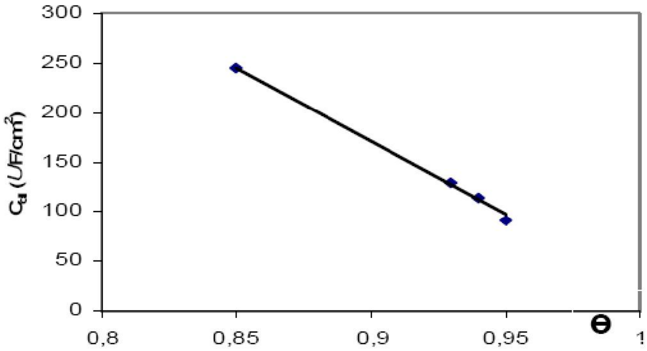

Figure 11 : The double layer capacitance as function of the surface coverage

strong adsorption on the active sites of the electrode surface, and the formation of thicker adsorption layer. Also the linear decease of C_{dl} with the surface coverage θ means that the capacitance contribution from the inhibitor covered surface is solely due to the adsorbed molecules at low surface coverage (Figure 11)[54].

CONCLUSIONS

The results of experimental studies showed that the pigment extracted from reddish prickly pear juices act as a good inhibitor for 316L stainless steel in 30% H_3PO_4 solution. The inhibition efficiency of pigment extracts increases with the concentration to attain a maximum value 97% at 1mL of pigment extract.

The inhibition action of the extracts was attributed to the physical adsorption of its compounds, mainly betanin and indicaxatin, onto the steel surface. We revealed also that the extract acts as a mixed inhibitor.

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