



A Moroccan *Opuntia Ficus Indica* methanolic flowers extract as an eco-friendly antioxidant and anti-corrosion for mild steel in 1 M HCl

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Abstract

Antioxidant and anti-corrosion activities of the methanolic extract of *Opuntia ficus indica* flowers from Morocco were investigated in this study. The mineral composition of *Opuntia ficus indica* flowers shows that sodium was the predominant metal followed by K, Mg, P, Mn, Zn, Cu, Fe, Cr and Ni. Results showed that *Opuntia ficus indica* methanolic flowers extract has the most effective antioxidant capacity in scavenging DPPH radicals. Also, this extract was investigated as a green corrosion inhibitor for mild steel in 1 M HCl solution using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Polarization curves reveal that the investigated methanol extract is a cathodic behavior. The inhibition efficiency increased with the increase in the concentration of the extract. It was found that the adsorption of the inhibitor on mild steel surface obeys the Langmuir's adsorption isotherm. The results obtained from weight loss and electrochemical techniques are in good agreement.

Keywords: *Opuntia ficus indica*; Mineral composition; Antioxidant activity; Anticorrosive activity.

1. Introduction

Opuntia ficus indica derived from Cactaceae family that grows in arid and semi-arid regions of the world is widely distributed in Mexico, Latin America, Australia, South Africa, and the whole Mediterranean area. In these populations, the cactus cladodes, fruits and flowers are featured for their interesting contents of antioxidants, pectin polysaccharides, phenolic compounds, vitamins and minerals [1].

The flowers of *Opuntia ficus indica* were used for medical purposes and as oxidants. The antioxidant and anti-ulcerogenic activities of a 50% methanolic extract of *Opuntia inermis* flowers which were evaluated in vivo for the ability to prevent ethanol-induced gastric ulcer in rats [2]. Recently, the results of a study concerning the antioxidant and antibacterial activities of *Opuntia* flower extracts and the ability to enhance wound healing were published in 2015 [3].

Natural products as corrosion inhibitors for various metals have been widely studied by several authors [4-8]. The metal corrosion inhibition activity of plant extracts can be attributed to the presence of heterocyclic compounds like alkaloids, flavonoids, and other compounds such as tannins, cellulose and polycyclic compounds. These compounds form a thin on the metal surface, thus preventing corrosion.

The objectives of this study were firstly to determine the mineral composition of *Opuntia ficus indica* flowers. Secondly, to evaluate the antioxidant activities using two in vitro tests; DPPH radical scavenging activity and carotene bleaching assays of the methanol extract of *Opuntia ficus indica*, and investigate it as a green corrosion inhibitor for mild steel in 1 M HCl solution. The study is conducted by weight loss, polarization curves, and electrochemical impedance spectroscopy methods.

2. Materials and methods

2.1. Material

Flowers of *O. ficus indica* were collected from Oujda, Morocco, in May 2015 (Figure 1). The fresh flowers were then air-dried at 25 °C, powdered and stored until use. Hexane was purchased from (E. Merck). 2, 2-Diphenyl-1-picrylhydrazyl (DPPH) and ascorbic acid were purchased from (Sigma-Aldrich GmbH, Germany). All other chemicals and solvents were of the highest analytical grade and used as supplied.

2.2. Extraction procedure

The flowers were dried and ground to get fine powder. Twenty grams of the fine powder were extracted with 150 mL solvent. Hexane and methanol were used as solvents in this study.



Figure 1: *Opuntia ficus indica* flowers

2.3. Maceration extraction (ME)

The powdered flowers samples were left to macerate for 2 hours under stirring with n-hexane at room temperature. After maceration, the extract was filtered through filter paper and the solvent was evaporated using a rotary evaporator.

2.4. Extraction with methanol

100 ml of methanol was added to the defatted residue. The mixture was stirred for 24 hours at room temperature, centrifuged at 4500 round per minute for 10 minutes and lyophilized. The methanolic flowers extract (MFE) yielded 11.82 g of yellow residue and was stored at 4 °C for later use.

2.5. Mineral composition analysis of *O. ficus indica* flowers

A mass of 150 mg of flowers was dried and ground. Mineral analysis was carried out by using 2 mL of nitric acid (70%), 3 mL of hydrofluoric acid and 2 mL of hydrochloric acid. The mixture was then boiled at about 100-110 °C for 15 hours. After cooling, 25 mL of 2M HCl solution was added to the mixture. The Minerals content was determined using an inductively coupled plasma atomic emission spectrometer (Ultima 2 - JobinYvon).

2.6. Antioxidant activity evaluation: DPPH assay

The antioxidant activity was assessed using 2, 2-diphenyl-1-picrylhydrazyl (DPPH) radical-scavenging assay and ascorbic acid bleaching test. It is strongly correlated to the phenolic compounds [9,10]. 0.1 mL of various concentrations of (MFE) extract (10, 50, 100, 200, 500, and 1000 µg/mL) was added to 3.9 mL of a 0.004% methanolic solution of DPPH. After 30 minutes incubation period at room temperature, the absorbance was measured at 517 nm against a blank. The antioxidant activity of MFE was calculated as an inhibitory effect (IE %) of the DPPH radical formation as follows:

$$I\% = [(A_{\text{blank}} - A_{\text{sample}}) / A_{\text{blank}}] \times 100 \quad (1)$$

Where, A_{blank} is the absorbance of the control reaction (containing all reagents except the extract), and A_{sample} is the absorbance of the solution containing the extract.

The DPPH radical-scavenging activity was estimated from the difference in absorbance, with or without tested extract, and expressed as a percentage of DPPH scavenged in solution. The IC₅₀ value represents the concentration of an individual compound required to quench 50% of DPPH under experimental conditions. All the tests were done in triplicate.

2.7. Anti-corrosion properties of MFE

2.7.1. Sample and solution preparation

The composition of mild steel specimens was as follows: 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S and 99.21% Fe. Specimens were polished using emery paper of grade ranging from N°400 to N°1200; and then rinsed with distilled water, degreased with acetone and dried with warm air before use.

Different inhibitor concentrations (0.125, 0.25, 0.5 and 1 g/L) were prepared from the methanolic flowers extract in 100 mL of 1 M HCl with stirring at room temperature. 100 mL of 1 M HCl without inhibitor was used as blank test solution.

2.7.2. Weight loss, polarization and EIS measurements

Weight loss measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 ml. The used steel specimens had square shape with the following dimensions (1.5 cm x 1.5 cm x 0.05 cm). They were immersed in the tested extract for 6 hours at 35°C. After that, the specimens were carefully washed with double-distilled water, dried and then weighed. From the weight loss measurements, the corrosion rate expressed in $\text{mg cm}^{-2} \text{h}^{-1}$ was calculated.

Electrochemical measurements were carried out in a conventional three-electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) in the form of disc cut from mild steel has an area of 1 cm^2 and was embedded in polytetrafluoro ethylene. A saturated calomel electrode (SCE) and a disc platinum electrode were used, respectively, as reference and auxiliary electrodes. The temperature was thermostatically controlled at $35 \pm 1^\circ\text{C}$.

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltmaster soft-ware. This potentiostat was connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. The potential was stabilized at free potential for 30 minutes before any run. The polarization curves are obtained from -800 mV to -200 mV at 308 K. The solution test was de-aerated by bubbling nitrogen. The electrochemical impedance spectroscopy (EIS) measurements were carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at E_{corr} . 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 30 minutes of exposure at 308 K. The impedance diagrams are shown in the Nyquist representations. Experiments were repeated three times to ensure the reproducibility of results.

3. Results and discussion

3.1. Mineral composition of *O. ficus indica* flowers

The mineral content of *O. ficus indica* dry flowers was determined and given in (Table 1).

The results of (Table 1) show some nutritionally important minerals (K, Mg, Na, P, Fe, Zn, Cu, Mn, Cr and Ni) for *O. ficus indica* flowers. The content of these minerals is one of the most essential aspects that influence the use of edible flowers in human nutrition. *Opuntia* flowers were considered as a good source of minerals [11]. Sodium (Na) was the predominant mineral with (20.19 g/kg of dry flowers) followed by potassium (K) with (16.73 g/kg), magnesium (Mg) with (5.48 g/kg) and phosphorus (P) with (3.37 g/kg). These results are in relative agreement with those reported by M. Ennouri et al. [11] and I. Ammar et al. [12]. The value of sodium content is higher in this study. The sodium content is of interest; it is beneficial for people with kidney problems and hypertension [10, 13-14]. The difference in the minerals amounts reported by authors in different countries could be attributed to the type of *Opuntia* and the climatic conditions where the plants grow, such as rain precipitation or availability of irrigation.

Table 1: The mineral composition of *O.ficus indica* dry flowers.

	Mineral	This study (g/Kg dry flowers)	Literature (g/Kg dry flowers)	
			[11]	[12]
Major elements	K	16.73	22.78 ± 0.164	16.12 ± 0.44
	Mg	5.48	4.294 ± 0.102	3.58 ± 0.84
	Na	20.19	1.372 ± 0.043	0.83 ± 0.07
	P	3.37	–	–
Minor elements	Fe	0.039	0.095 ± 0.021	0.13 ± 0.01
	Zn	0.089	0.036 ± 0.08	0.07 ± 0.01
	Cu	0.071	–	–
	Mn	0.33	–	–
	Cr	0.024	–	–
	Ni	0.013	–	–

3.2. DPPH Radical Scavenging and Antioxidant Activities of MFE

The radical scavenging activity of MFE and ascorbic acid on DPPH radicals increased significantly with increasing the concentration of the MFE from 10 to 1000 µg/ml as shown in (Figure 2).

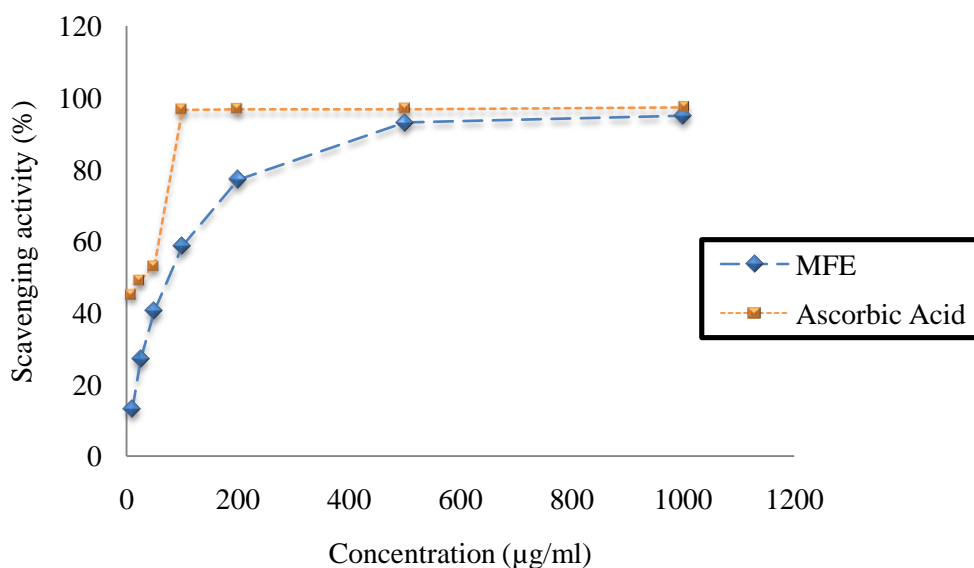


Figure 2: Antioxidant activity of methanolic flowers extract (MFE) and ascorbic acid determined by DPPH radical scavenging assay.

The results presented in (Table 2) revealed that the methanol extract displayed significant antiradical activity, with IC50 value of 98µg/mL. Ascorbic acid showed the highest DPPH radical scavenging activity (IC50 value of 32.57 ± 1.98µg/mL).

Table 2: Antioxidant activity of methanolic flowers extract (MFE) and ascorbic acid determined by DPPH radical scavenging assay.

Inhibition ratio (%)		
C (µg/mL)	methanolic flowers extract (MFE)	Ascorbic acid
10	13.14	45.28
25	27.14	49.3
50	40.57	59.2
100	58.68	96.6
200	77.11	96.75
500	93.15	96.81
1000	95	97.30
Equations	0.2709x + 23.44	0.2778x + 40.948
Coefficient R ²	0.9831	0.997
IC ₅₀ (n=3)	98.04 ± 8.89	32.57 ± 1.98

Similar results on the antioxidant activity of methanolic extract of *O. ficus indica* and *O. ficus indica* inermis flowers showed IC₅₀ values of 100 and 147 µg/mL, respectively [15, 2].

The DPPH free radical scavenging model can be used to evaluate the antioxidant activity in a relatively short time. The decreased absorbance results in a color change from purple to yellow, as radicals were scavenged by antioxidants through the donation of hydrogen to form the stable DPPH molecule [16, 17]. The antioxidant activity detected for the methanol extract from *O. ficus indica* flowers could be attributed to the hydrogen donating effect of phenolic compounds and flavonoids [2, 18]. Consumption of foods rich in natural antioxidants has been reported as being protective against certain types of cancer and may also reduce the risk of cardiovascular and cerebrovascular events [10, 19].

3.3. Weight loss measurements

Weight loss measurements were carried out on mild steel in 1 M HCl solution in the absence and presence of different concentrations of MFE and are shown in Figure (3). The calculated inhibition efficiency (E_w %) values are listed in (Table 3). From this table, it is noted that the E_w % increases steadily with increasing of the MFE concentration. The inhibition efficiency (E_w %) and surface coverage (θ) were calculated using the following equation:

$$E_w (\%) = \frac{W_0 - W_i}{W_0} \times 100 \quad (2)$$

Where, w_0 and w_i are the weight loss values in the absence and presence of MFE.

The observed inhibition action of the MFE may be attributed to the adsorption of its components on mild steel surface. The adsorbed layer isolates the metal surface from the aggressive acidic media and limits its dissolution by blocking of its corrosion sites [20]. It is clearly noticed from (figure 3), that the corrosion rate decrease as the concentration of MFE increasing. On the other hand the inhibition efficiency increases as the concentration of MFE increasing. The inhibition efficiency (E_w %) reaches a value of 94% at a concentration of MFE (1g/L).

3.4. Adsorption Isotherm

The adsorption isotherms can provide significant information about the interaction of the MFE compounds and the mild steel surface. Two main types of interaction can be used to show the adsorption behavior of the MFE: chemisorption and physisorption. This method relies on the chemical structure of the MFE compounds as well as the electrochemical potential, the charge and nature of the mild steel [21, 22]. The adsorption of inhibitor molecules from aqueous solution can be considered a quasi-replacement between the inhibitor compounds dissolved in the aqueous phase, $Org(sol)$, and x of H_2O molecules adsorbed on the metal surface, $H_2O(ads)$, where x is the number of H_2O molecules substituted by the inhibitor. In this case, the adsorption of the inhibitor

required the desorption of H₂O from the surface of mild steel. Langmuir adsorption isotherm can be expressed by the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (3)$$

Where, C is the concentration of inhibitor, K the adsorption equilibrium constant, and θ is the surface coverage.

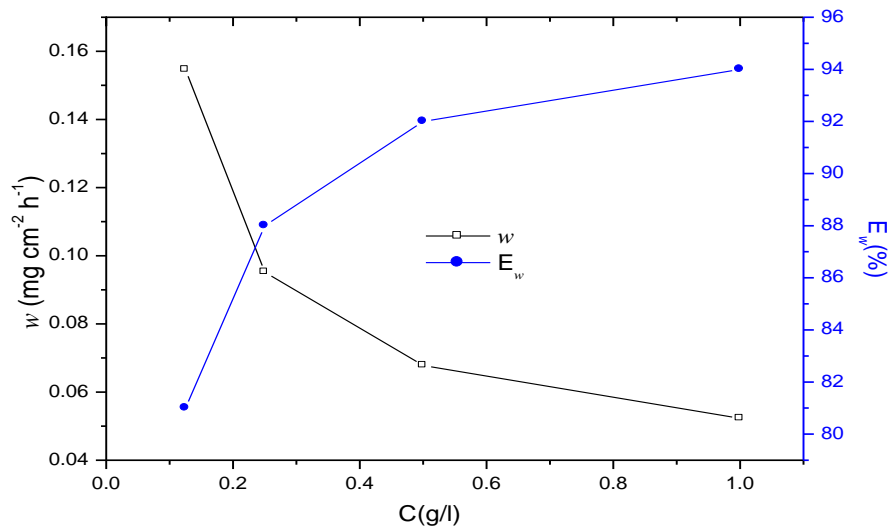


Figure 3: Variation of inhibition efficiency and corrosion rate of mild steel in 1M HCl solution without and with different concentrations of MFE.

Table 3: The corrosion rate (w) in ($\text{mg cm}^{-2} \text{h}^{-1}$) and inhibition efficiency (E_w %) data for mild steel in 1 M HCl solution without and with various concentrations of MFE at 35 °C.

Inhibitor	Concentration (g/L)	W ($\text{mg.cm}^{-2} \text{h}^{-1}$)	E_w (%)
1 M HCl	-	0.8200	---
MFE	1.000	0.0523	94
	0.500	0.0678	92
	0.250	0.0952	88
	0.125	0.1546	81

Plots of C_{inh}/θ as a function of C_{inh} yielded a straight line, as shown in (Figure 4). The linear regression coefficient (R^2) is almost equal to 1 ($R^2 = 0.9999$), and the slope is nearly 1, indicating that the adsorption of MFE on the mild steel surface is very well described by the Langmuir adsorption model.

3.5. Polarization curves

Figure (5) shows potentiodynamic polarization curves recorded for mild steel in 1 M HCl solutions in the absence and presence of various concentrations of the MFE at 35°C. Lee and Nobe [23] reported the occurrence of a current peak between the apparent-Tafel and limiting-current regions during potential sweep experiments. The presence of MFE shifts both anodic and cathodic branches to the lower values of corrosion current densities and thus causes a remarkable decrease in the corrosion rate. The parameters derived from the polarization curves in (Figure 5) are given in (Table 4).

Inhibition efficiency (E_p %) is defined in the following equation:

$$E_p\% = \frac{i_{\text{cor}}(0) - i_{\text{cor}}(\text{inh})}{i_{\text{cor}}(0)} \times 100 \quad (5)$$

Where, $i_{\text{corr}}(0)$ and $i_{\text{corr}(\text{inh})}$ represent corrosion current density values without and with inhibitor, respectively.

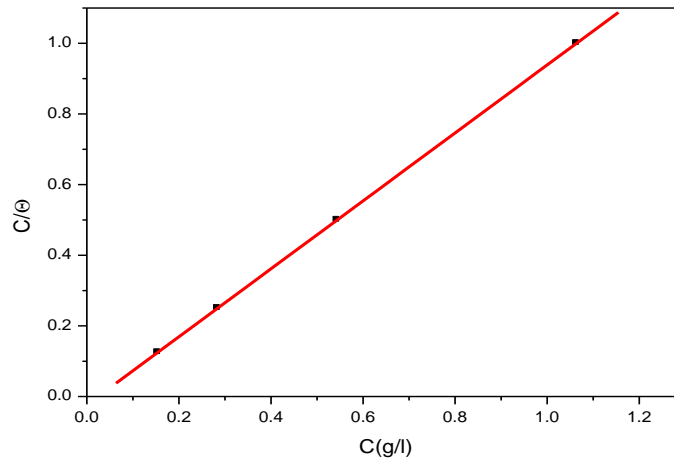


Figure 4: Langmuir adsorption plot for mild steel in 1 M HCl solution containing MFE at 35 °C.

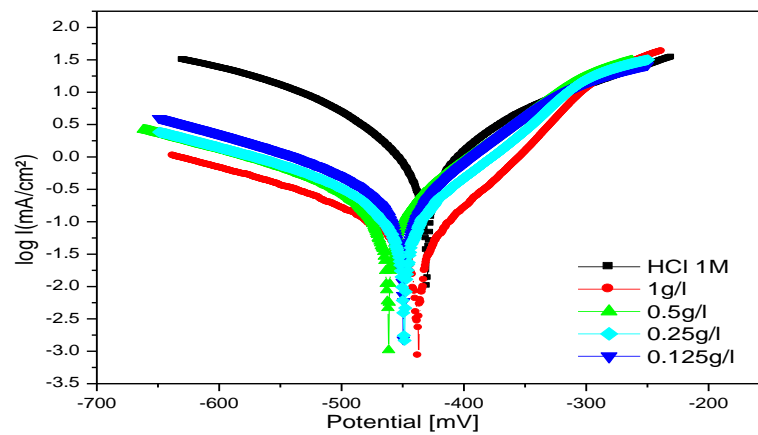


Figure 5: Potentiodynamic polarization curves for the corrosion of mild steel in 1 M HCl solution without and with various concentrations of MFE at 35 °C.

In 1M HCl solution, the presence of MFE causes a remarkable decrease in the corrosion rate i.e., shifts both anodic and cathodic curves to lower current densities. In other words, both cathodic and anodic reactions of mild steel electrode are retarded by MFE in 1M HCl solution. The Tafel slopes of β_c at 35 °C do not change remarkably upon addition of MFE, which indicates that the presence of MFE does not change the mechanism of hydrogen evolution and the metal dissolution process. Generally, an inhibitor can be classified as cathodic type if the shift of corrosion potential in the presence of the inhibitor is more than 85 mV with respect to that in the absence of the inhibitor [24-27]. In the presence of MFE, E_{corr} shifts to less negative but this shift is very small (about 7- 60 mV), which indicates that MFE can be arranged as anodic inhibitor.

Table 4: Effect of concentration of MFE on the electrochemical parameters calculated using potentiodynamic polarization technique for the corrosion of mild steel in 1 M HCl at 35 °C.

Inhibitor	Concentration (g/L)	$-E_{corr}$ (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	$-\beta_c$	E_p (%)
1 M HCl	--	429	1788	151	--
MFE	1.000	436	53	106	97
	0.500	461	126	146	93
	0.250	488	242	199	86
	0.125	449	355	189	80

3.6. Electrochemical impedance spectroscopy measurements

The impedance behavior of the mild steel electrode in the presence of MFE is shown in Figure (6) in Nyquist representations. Nyquist plots of the mild steel electrode in 1 M HCl solution are given as an inset in the same figure. The corrosion of mild steel in 1 M HCl solution is mainly controlled by the charge transfer process. The addition of MFE to the 1 M HCl solution does not change the shapes of the Nyquist plots. However, the diameter of the capacitive loop gradually increases with increasing concentrations of the inhibitor, indicating the adsorption of inhibitor molecules on the metal surface making a barrier and protect the metal surface from aggressive attack by the solution [28-30]. As seen from the Nyquist plots (**Figure 6**), maximum corrosion prevention was observed at the concentration of (1g/L) MFE.

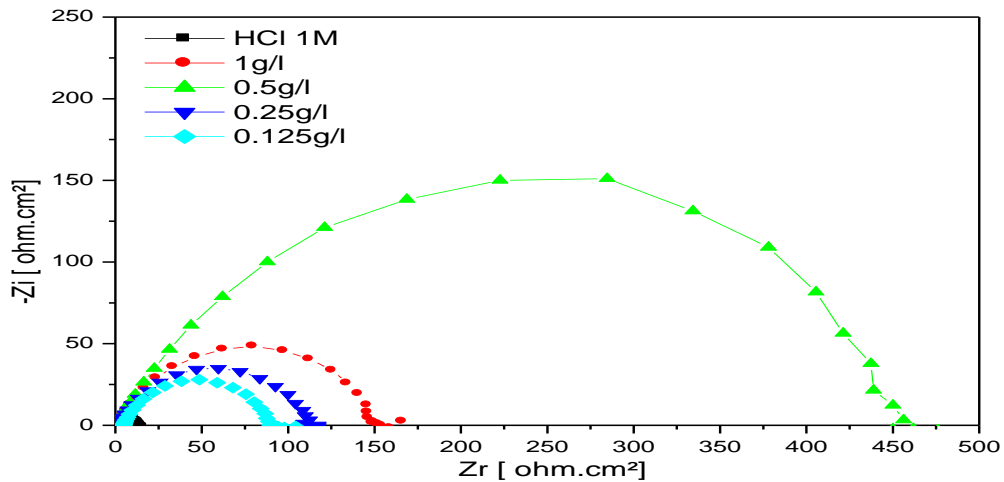


Figure 6: Nyquist plots for mild steel in 1 M HCl solution in the absence and presence of various concentrations of MFE at 35 °C.

The main parameters deduced from the analysis of Nyquist diagram are:

- The resistance of charge transfer R_{ct} (diameter of high frequency loop)
- The capacity of double layer C_{dl} which is defined as follows:

$$C_{dl} = Y_0 (\omega_{max})^{n-1} \quad (6)$$

Where, ω_{max} (rad s^{-1}) is the angular frequency corresponding to the maximum value of imaginary impedance. Since the electrochemical theory assumed that $(1/R_{ct})$ is directly proportional to the capacity of double layer C_{dl} , the inhibition efficiency (%E) of the inhibitor for mild steel in 1 M HCl solution was calculated from R_{ct} values obtained from impedance data at different inhibitor concentration using the following equation:

$$E\% = (1 - R_{ct}^0/R_{ct}) \times 100 \quad (7)$$

Where, R_{ct}^0 and R_{ct} are the charge transfer resistance in the absence and presence of MFE extract, respectively. The inspection of the (**Table 5**) shows clearly that R_{ct} and C_{dl} values have opposite trend at the whole concentration range. The R_{ct} increases while the C_{dl} decreases with the increase of MFE concentration. A large R_{ct} is associated with a slower corroding system [31, 32]. Furthermore, the decrease in the C_{dl} with the increase of MFE concentration may be attributed to the formation of a protective layer on the mild steel surface [33, 34].

Table 5: Impedance parameters and inhibition efficiency values for mild steel immersed for half an hour in 1 M HCl solution containing different concentrations of MFE at 35 °C.

Inhibitor	Concentration (g/L)	R_{ct} ($\Omega \cdot \text{cm}^2$)	C_{dl} ($\mu\text{f}/\text{cm}^2$)	E (%)
1 M HCl	-	15	200	--
MFE	1.000	455	55	97
	0.500	151	57	90
	0.250	112	67	87
	0.125	85	118	82

The experimental data were fitted by a Zview software. The electrical equivalent-circuit diagram corresponds to the metal/solution interface (double layer between the mild steel surface and acid solution) was shown in (Figure 8).

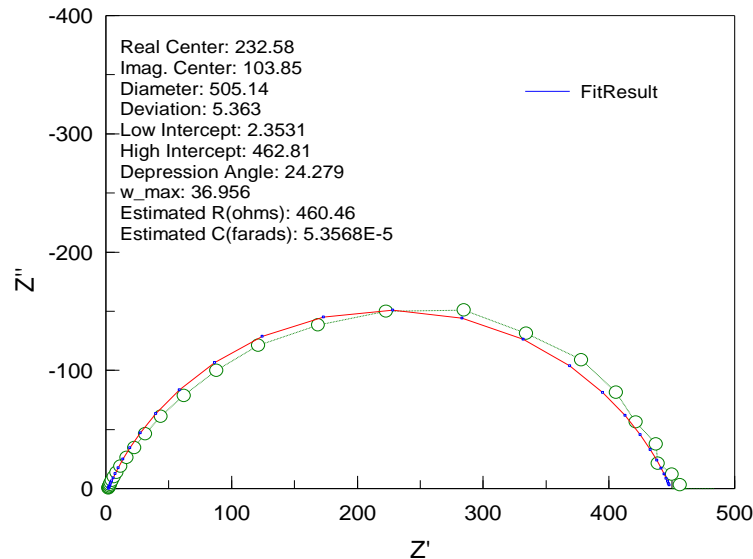


Figure 7: EIS Nyquist diagram for mild steel/1 M HCl + 1g/L of MFE interface: (...) experimental; (-----) fitted data using the model in (Figure 8).

In this equivalent circuit, R_u is the solution resistance, R_{ct} present the charge transfer resistance whose value is a measure of electron transfer across the surface and CPE is the constant phase element. The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor in order to take into account the electrode surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [35, 36] and therefore to give a more accurate fit [37]. The impedance of the CPE is expressed as [38, 39]:

$$Z_{CPE} = [Y_o (j\omega)^{-n}]^{-1} \quad (8)$$

Where, Y_o is proportionality coefficient, ω is the angular frequency and $j^2 = -1$ is the imaginary number. Numerous authors have used CPE in modeling by relating it to different physical phenomena [40]. The experimental data were very well fitted (Figure 7) according to the proposed equivalent circuit as shown in (Figure 8). This model is valid for all concentrations of MFE and it is well representative of the phenomena which may occur in the investigated mild steel MFE/HCl system, both in the HF and in the LF parts of the spectra

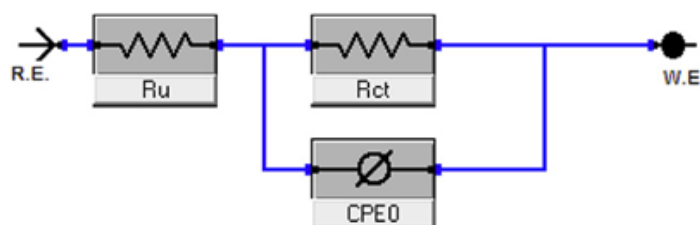


Figure 8: Electrical equivalent circuit diagrams used as a model for metal/solution interface.

Conclusion

The results presented in this study are the first information on the mineral composition, antioxidant and anti-corrosive activities of methanolic *Opuntia ficus indica* flowers extract. This study showed that *Opuntia ficus indica* flowers were rich in macroelements. Cactus flowers were considered as a good source of minerals. The present study evaluated the in vitro DPPH radical antioxidant scavenging and anti-corrosion properties of methanolic flowers extract. This extract presented a strong antioxidant activity. Results obtained through weight

loss measurements and electrochemical tests demonstrated that methanolic flowers extract was an efficient eco-friendly green corrosion inhibitor for mild steel in 1 M HCl solution. The information presented in this study supports that this extract may be considered as a good source of minerals, and as an excellent antioxidant and a green corrosion inhibitor for metals.

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