Experimental and Computational Simulation (DFT approach) evaluation of Nopal extract as green corrosion inhibitor for mild steel in 1M HCl

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ABSTRACT

The effect of Nopal (*Opuntia ficus-indica*) as green corrosion inhibitor for mild steel in 1M HCl solution have been investigated by using Weight Loss Measurements (WLM) and Electrochemical Impedance Spectroscopy (EIS) measurement. Also, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR). The inhibitor concentrations used ranged from 0, 50, 75, 100, 150, 200 and 300ppm at 25 and 40°C. The inhibition behavior has been associated with adsorption effects for inhibitors. In fact, the adsorption of the inhibitor on the steel surface follows the Langmuir adsorption isotherm. Computational Simulation by using the Density Functional Theory (DFT) with Gaussian 09 program and the B3LYP/6-31G(d) in the presence the solvent IEFCPCM/water, level of theory was further used to calculate some electronic properties of the molecule (Pectin) in order to ascertain any correlation between the inhibitive effect and molecular structure of Nopal (*Opuntia ficus-indica*) extract.

Key words: Inhibitor, Corrosion, Computational Simulation,

INTRODUCTION

The protection of metal against corrosion is a major industrial problem. Mild steel has been the most widely used alloy for structural and industrial applications such as, industries mining, construction and metal processing equipment [1]. The use of inhibitors is one of the best options of protecting metals against corrosion in acid solutions. The new generation of environmental regulation requires the replacement of toxic inhibitors with nontoxic inhibitors [2]. An immense number of scientific studies have been devoted to the inhibitive action of green inhibitors on the corrosion of mild steel in acidic solutions, showing that these extracts could serve as good corrosion inhibitor; the cited extracts include extracts of *Punica granatum* [3], *Nicotina tabacum* leaves extract [4], *Chenopodium Ambrosioides* extract [5], Red Apple extract [6], *Ginkgo* leaves extract [7], *Medicago-sative* extract [8], *Murraya-koenigii* extract [9], *Spirulina-platensis* extract [10]. Thus, the aim of this work, is to gain some insight in the corrosion resistance of carbon steel immersed in acid chloridric in presence of Nopal (*Opuntia ficus indica*). The antioxidant activity of Nopal extract has due to the presence the phenolics compounds, flavonols, pectin, kaempferol, luteilin, quercitrin and rutin [11]. Therefore, in keeping with the previous study on chemical composition, this present study report a comparison of experimental technical with investigation theoretical of Pectin molecule present in the Nopal (*Opuntia ficus-indica*) extract. Recently, there is a substantive effort in the literature especially on the use of Density Functional Theory (DFT) as a powerful theoretical tool in analyzing inhibitor/surface interaction. In agreement with the DFT, the energy of the fundamental state of a polielectronic system can be expressed through the total electronic density, and in fact the use of the electronic density instead of the wave function for the calculation of the energy constitutes the fundamental base of DFT [12].

EXPERIMENTAL PROCEDURE

Material Preparation

The mild steel specimens of composition C=0.15%, Mn=0.70%, P=0.010%, S=0.027%, Cr=0.016%, Ni=0.12%, Al=0.006%, Cu=0.044% and the balance Fe. The bar of mild steel with diameter of 1 cm was cut off in section of 1 cm for weight loss study. The specimens were polished successively by use of SiC papers of 100 until 800 grade; and then thoroughly cleansed with distilled water and then with ethanol. While coupons of size 0.7850 cm^2 were used for electrochemical studies. It was encapsulated in commercial epoxy resin.

Inhibitor Preparation

50 g of Nopal fresh were soaked in 100 ml using double distilled water and refluxing the solution for one hour. After cooling, solutions were filtered followed by drying in vacuum oven for one night (lyophilized). The extract solid was used as a corrosion inhibitor.

Solution Preparation

The corrosive medium was 1M HCl prepared with 38% analytical grade supplied by Sigma-Aldrich. Double distilled water was used for the preparation of all reagents.

Weight Loss Measurements

Mild steel specimens were immersed in 50 ml of 1M HCl with various extract concentrations (0, 50, 75, 100, 150, 200 and 300ppm) for time of exposition of 4.5, 6.5, 12, 24, 48 and 120 hours. After a total time of exposition specimens were taken out, washed with double distilled water, degreased with methanol, dried and weighted accurately. The weight loss (in grams), was taken as the difference in the weight of the mild steel specimens before and after immersion in different test solutions. The test was performed in triplicate to guarantee the reliability of results, and the mean value of the weight loss is reported. Tests were performed at room temperature 25 and 40ºC by using a hot plate. Corrosion rates, in terms of weight loss measurements, ΔW, were calculated as follows:

$$\Delta W = (m_1 - m_2) / A \quad (1)$$

were m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after corrosion, and A the exposed area of the specimen. For the weight loss test, inhibitor efficiency (IE) was calculated as follows:

$$IE (\%) = 100 (\Delta W_1 - \Delta W_2) / \Delta W_1 \quad (2)$$

were ΔW_1 is the weight loss without inhibitor, and ΔW_2 the weight loss with inhibitor.

Electrochemical techniques

The electrochemical experiments were performed using a typical three electrode cell (A platinum rod was used as counter electrode and saturated calomel electrode (SCE) as reference electrode) at room temperature (25 and 40ºC) and naturally aerated conditions. The impedance studies were carried out using AC signals of 10mV amplitude for the frequency spectrum from 100 MHz-100Kz. The charge transfer resistance values were calculated from the diameter of the semi-circles of the Nyquist plots. The impedance studies were studied using Solartron Impendace / Gain-Phase analyzer SI 1260. The corrosion inhibition efficiency (%) was determined by equation (3), where Rct_1 and Rct_2 are the charge transfer resistances in presence and absence of inhibitor.

$$IE (\%) = 100 (Rct_2 - Rct_1) / Rct_2 \quad (3)$$

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectrum was recorder with a frequency ranging from 4000 to 700 cm^{-1} for the solution of the Nopal extract in 1M HCl and specimen. The immersed was for 12 hours in 40ºC. After solvent evaporation, the surface film was scraped carefully and its FT-IR spectra were recorded using Perkin Elmer model spectroscopy.

Scanning electron microscope studies (SEM)

Mild steel specimens were immersed in a corrosive environment of 1M HCl having an optimum concentration (300ppm) of the Nopal extract for 12 hours at 40ºC. At the end of the experiment, the specimens were washed with distilled water, dried, and examined for their surface morphology using JEOL-JSM5800LV model scanning electron microscope.

Computational Details

Density Functional Theory (DFT) methods have become very popular in the last decade due to their accuracy and less computational time [13]. The geometry optimization together with the vibrational analysis of the Pectin was carried out at the B3LYP/6-31(d) level, using Gaussian 09 program. The properties of the molecule were calculated for molecule neutral. It is well known that the phenomenon of electrochemical corrosion occurs in liquid phase. As a result, it was necessary to include the effect of solvent in the computational calculations. In the Gaussian 09 program, IEFCPCM/water methods were used to perform.

Within the framework of density functional theory, the electronegativity (X) [14]:

$$X = -(\partial E / \partial N) \quad (4)$$

and hardness (η) is defined as [14]:

$$\eta = 1/2\ (\partial^2 E / \partial N^2) \qquad (5)$$

were E is the electronic energy and N is the number of electrons.

I and A are related in turn to HOMO and LUMO, using the equations 6 and 7 [16].

$$I = -\ HOMO \qquad (6)$$
$$A = -\ LUMO \qquad (7)$$

These quantities are related to electron affinity (A) and ionization potential (I) using the equations 8 and 9.

$$X = (I + A) / 2\ , \quad X = -\ (LUMO + HOMO) / 2 \qquad (8)$$
$$\eta = (I - A) / 2\ , \quad X = -\ (LUMO - HOMO) / 2 \qquad (9)$$

The number of transferred electrons (ΔN) from the inhibitor molecule to the metal surface can be calculated by using the equation 10.

$$\Delta N = (X_{Fe} - X_{inh}) / [2(\eta_{Fe} + \eta_{inh})] \qquad (10)$$

where X_{Fe} and X_{inh} denote the absolute electronegativity of iron and the inhibitor molecule (Pectin) respectively; η_{Fe} and η_{inh} denote the absolute harness of iron and inhibitor molecule, respectively.

RESULTS

Weight Loss Measurements (WLM)

The effect of Nopal concentration in the weight loss measurements for the mild steel in 1M HCl at 25ºC and 40ºC are given in Figure 1. At 25ºC, the highest efficiency was obtained when 75ppm of Nopal was added, and then it decreased with a further increase in the inhibitor concentration. At 40ºC the efficiency values increased with the increase the Nopal concentration, the highest efficiency was obtained in 300ppm. Therefore, the efficiency increase with increasing the temperature. The increase in inhibitor efficiency is due to the increase in the number of constituent molecules of Nopal adsorbed on the metal surface at higher concentrations.

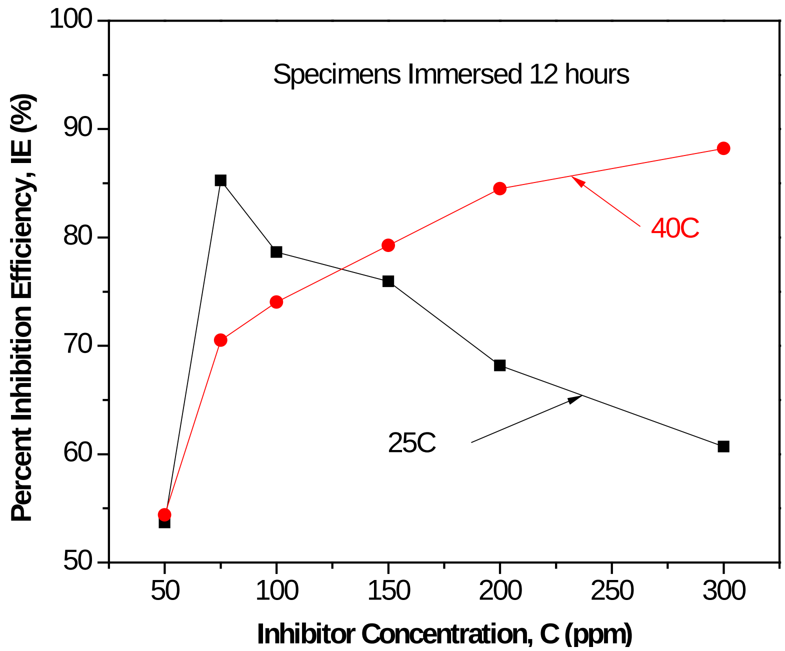

Figure 1. Inhibition efficiency of mild steel specimens in 12 hours the immersed in 1M HCl with Nopal extract using on the Weight Loss Methods at 25ºC and 40ºC.

The Table 1 shows the values of inhibition efficiencies at 25 and 40ºC.

Table 1. Values of inhibition efficiency (%) from weight loss measurement.

Inhibitor Concentration (ppm)	Inhibition Efficiency (%) In 25ºC	Inhibition Efficiency (%) In 40ºC
50	37	54
75	**87**	70
100	62	74
150	57	77
200	55	85
300	59	**89**

Electrochemical Impedance Spectroscopy (EIS)

The Figure 2 shows the representative Nyquist plots of mild steel obtained at 40ºC in 1M HCl solution in the absence and presence of various of various concentrations of Nopal (*Opuntia ficus-indica*) extract. In this temperature was obtained the highest efficiency. In The Nyquist plot of mild steel obtained in blank solution was magnified and added in Figure 2. The plots showed a depressed semi-circular shape. The efficiency values increased with the increase the Nopal concentration . This behavior indicates a process controlled by a charge transfer. The highest inhibitor efficiency (96%) was obtained by adding 300ppm.

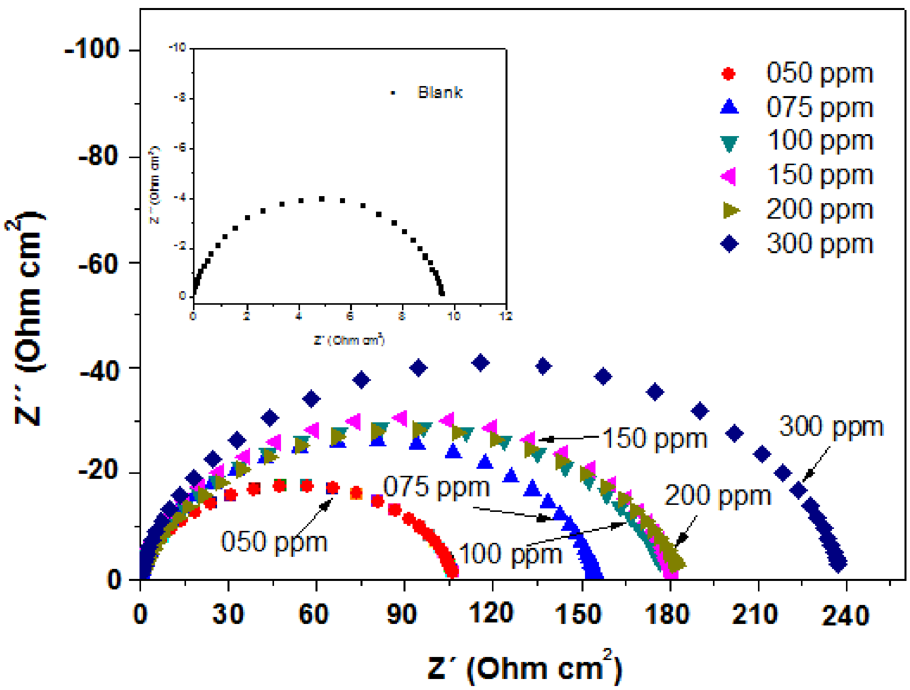

Figure 2. Nyquist plots of mild steel in absence and presence of Nopal extract at 40ºC in 1M HCl.

The impedance parameters derived from the Nyquist plots and percentage inhibition efficiency are given in Table 2. This shows that the *Rct* values increased and *Cdl* values decreased indicating a more controlled anodic and cathodic processes and the decrease in the capacitance values, which were attributed to the formation of the protective layer at the mild steel surface. To obtain the double layer capacitance (*Cdl*) values, the following equation was used:

$$Cdl = 1 / 2\pi f_{max} Rct \quad (11)$$

Table 2. Electrochemical impedance parameter values at 40ºC.

Concentration (ppm)	Rct (Ωcm^2)	Cdl ($\mu F\ cm^{-2}$)	Inhibition Efficiency (%)
0	10.75	1480.51	---
50	106.63	1257.15	90
75	155.45	1024.16	92
100	179.78	885.67	93
150	182.11	873.99	94
200	185.09	860.30	94
300	239.02	665.92	96

Fourier Transform Infrared Spectroscopy (FT-IR)

The Figure 3 shows the FT-IR spectrum of the extract at different concentrations. A strong and broad peak at 3000/3300cm^{-1} can be attributed to O-H stretching vibration. Before test, in 1718cm^{-1} is observed one peak corresponding C=O stretching vibration. The adsorption bands at 1616cm^{-1} were also observed for two test, this is due to N-H bending vibration. In 1402 and 1428cm^{-1} peaks were attributed at C-C stretching vibration (before and after respectively). A small peak at 1223cm^{-1} was observed after test, the peak increase before test, the peaks correspond to C-N stretching vibration. Peaks before and after in 1074 cm^{-1} attributed to C-O stretching vibration.

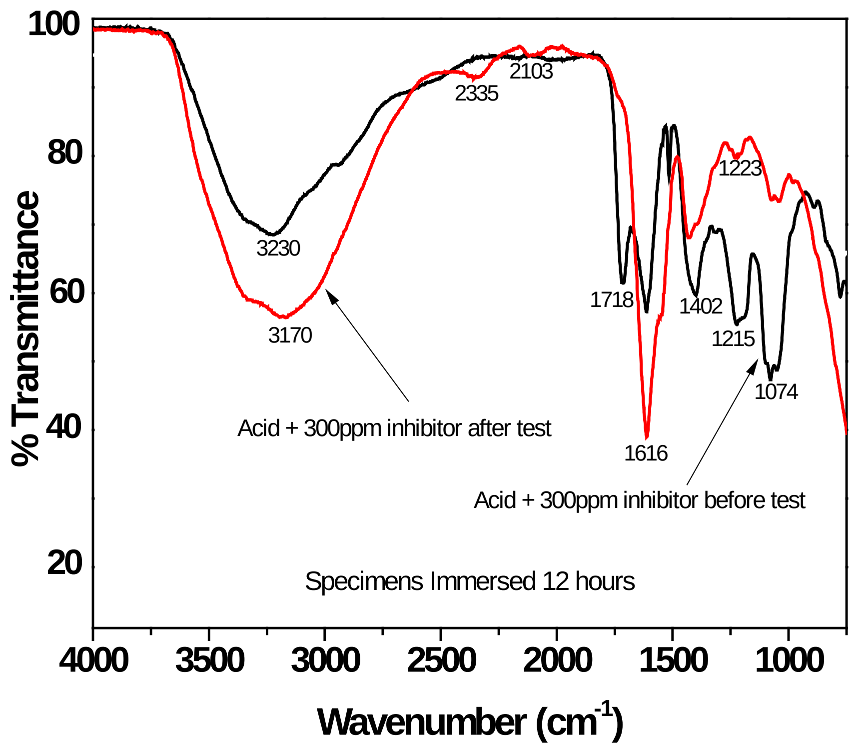

Figure 3. FT-IR spectrum of Nopal extract before and after corrosion test.

Thus, results showed that Nopal extract contain organic molecules that are rich in oxygen and nitrogen atoms as well as aromatic rings, which meet with the fundamental requirements of good inhibitor. A summary of these results is given in Table 3.

Table 3. Peaks from FT-IR spectra of Nopal extract before and after corrosion test and their identification.

Acid + 300ppm inhibitor before test		Acid + 300ppm inhibitor after test	
Frequency (cm^{-1})	**Functional group and vibration type**	**Frequency (cm^{-1})**	**Functional group and vibration type**
3230	O-H stretch	3170	O-H stretch
1718	C=O stretch	--	--
1616	N-H bending	1616	N-H bending
1402	C-C stretch	1428	C-C stretch
1215	C-N stretch	1223	C-N stretch
1074	C-O stretch	1074	C-O stretch

Adsorption Behavior

The adsorption behavior of Nopal (*Opuntia ficus-indica)* extract in 1M HCl solution, was obtained for the Langmuir isotherm model. The Langmuir adsorption could be represented by the following equation:

$$C / \theta = (1 / K) + C \qquad (12)$$

Where C is the concentration of inhibitor, θ is surface coverage and K is the adsorption constant. The surface coverage (θ) of the inhibitor on the mild steel surface is expressed by following equation:

$\theta = IE\ (\%) / 100$ (13)

The adsorption parameters, such as, regression coefficient (R^2), adsorption constant (K) and free energy of adsorption(ΔG) and slope values were obtained by straight line fitting between C/θ (y-axis) and C(x-axis). The Figure 4 shows the Langmuir isotherm of the polarization curves method.

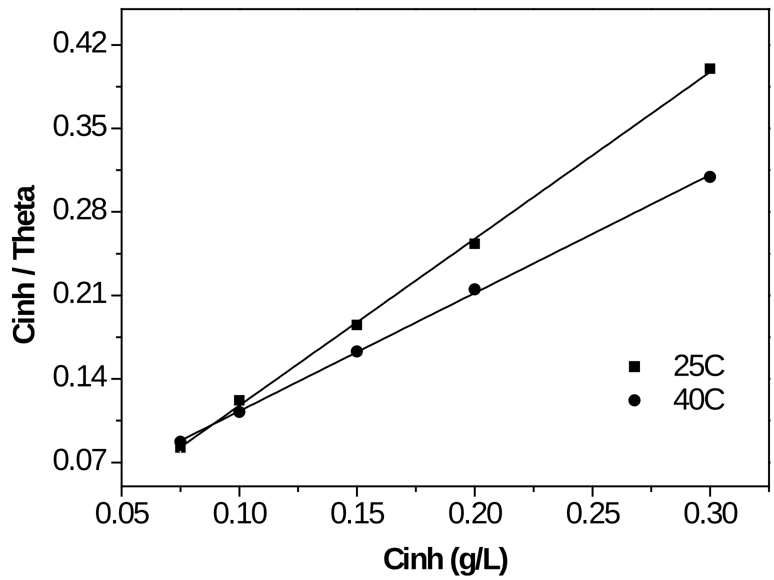

Figure 4. Langmuir isotherm for adsorption of Nopal extract on the mild steel surface.

The most important thermodynamic adsorption parameter is the free energy of adsorption (ΔG). The adsorption constant (K) is related to the standard free energy of adsorption, ΔG is calculated with the following equation:

$$\Delta G = -RTln(55.5K) \quad (14)$$

Where 55.5 is the water concentration of solution in mol/L. R is the ideal gas constant, T is the absolute temperature. Table 4 shows the values calculated in the Langmuir isotherm. The negative values of ΔG indicate the stability of the adsorbed layer on the mild steel surface and spontaneity of the adsorption process. Generally, the magnitude of ΔG around -20 kJ/mol or less negative is assumed for electrostatic interaction that exist between inhibitor and the charged metal surface (physisorption).

Table 4. Thermodynamic parameters for mild steel in 1M HCl in presence of the Nopal extract at different concentrations.

Isotherms	Temperature (ºC)	Slope	R^2	Kads	ΔG ads $KJ.mol^{-1}$
Langmuir	25	1.380	0.9986	55.50	-19.90
	40	0.014	0.9994	71.43	-21.56

Scanning Electron Microscope (SEM)

The scanning electron microscope images were recorded to establish the interaction of inhibitor with the metal surface. Figure 5A indicates the finely polished characteristic surface of mild steel. Figure 5B revealed that the surface was severely corroded due to the aggressive attack by 1M HCl. Figure 5C reveal the formation of a protective film by the inhibitor on the mild steel surface in acid medium. Figure 5B and 5C show specimens immersed 12 hours at 40ºC. The image 5C containing 300ppm of Nopal extract in 1M HCl.

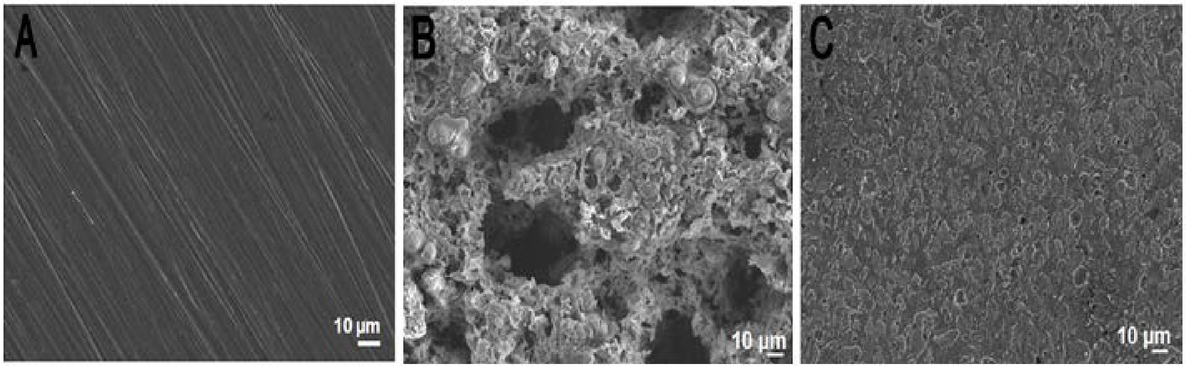

Figure 5. SEM images of (A) polished mild steel specimens. (B) mild steel specimens in HCl 1M. (C) mild steel specimens with Nopal extract in HCl 1M at 40ºC.

Computational Calculations

The inhibition effect of pectin (Figure 6) on the corrosion was studying. The calculations were performed optimized the pectin molecule, thus ensuring, having a structure in its minimum energy state (Figure 7). According to the frontier molecular orbital theory, the reactivity is a function of interaction between HOMO and LUMO levels of the reacting species. HOMO is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of HOMO is likely to indicate a tendency of the molecule to donate electrons. Therefore, the energy of the lowest unoccupied molecular orbital, LUMO, indicates the ability of the molecule to accept electrons. So, the lower the value of LUMO, the more probable the molecule would accept electrons. Thus the binding ability of the inhibitor to the metal surface increase with increasing of the HOMO and decreasing of the LUMO energy values. All the chemical parameters are given in Table 5.

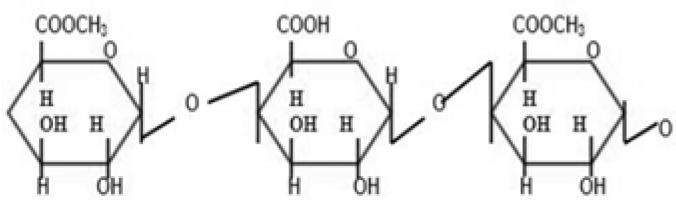
Figure 6. Chemical molecular structure of the Pectin.

Table 5. The calculated chemical parameters for Pectin using DFT at the B3LYP/6-31G(d) basis set in aqueous phase.

Chemical Properties	Values
HOMO (eV)	-0.17055
LUMO (eV)	-0.14206
ΔE	0.77526
Electronegativity (eV)	4.26
Hardness (eV)	0.36
Ionization Potential (eV)	4.59
Electron Affinity (eV)	3.92
Fraction of electrons transferred	-0.52

The separation energy (ΔE) is a important parameter and it is a function of reactivity of the inhibitor molecule toward the adsorption on metallic surface. As ΔE decreases, the reactivity of the molecule increases leading to increase in the inhibition efficiency of the molecule. This calculates present a ΔE=0.77526, increase the inhibition efficiency. Normally, with the least value of hardness (0.36) is expected to have the highest inhibition efficiency. Also, calculations showed an obvious correlation between the molecular weight and the inhibition efficiency (See Figure 6). The inhibition efficiency increase as the molecular weight. The number of electrons transferred (ΔN) show that the inhibition efficiency resulting from electron donation agrees with Lukovits´s study. If ΔN<3.6, the inhibition efficiency increases by increasing electron-donating ability to the metal surface.

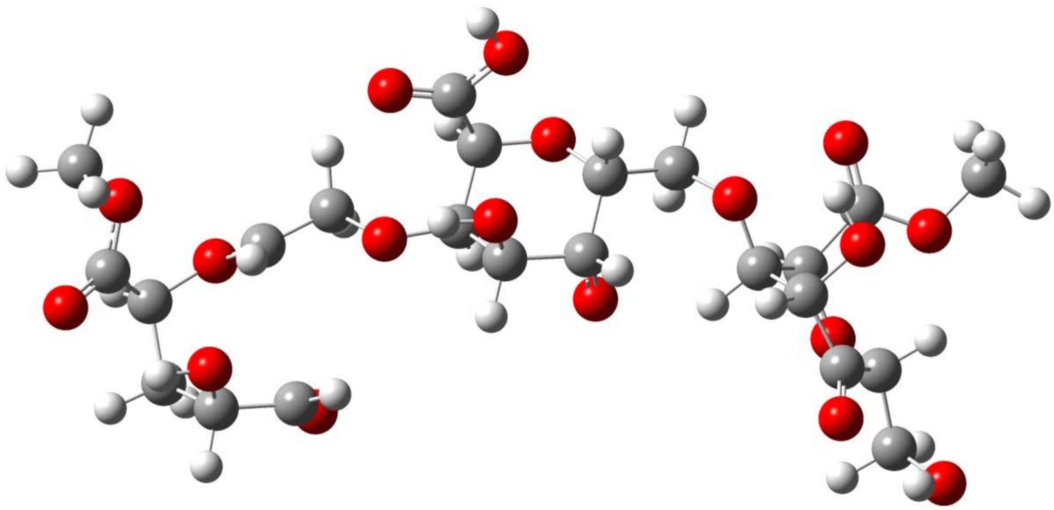

Figure 7. The optimized geometry of Pectin molecule.

Figures 8 and 9 show the HOMO and LUMO orbital contributions the studied molecules. The HOMO densities were concentrated on the ring in the central. For the LUMO distributions is modified towards right atoms. Thus, unoccupied orbitals of Fe atom can accept electrons from inhibitor molecule.

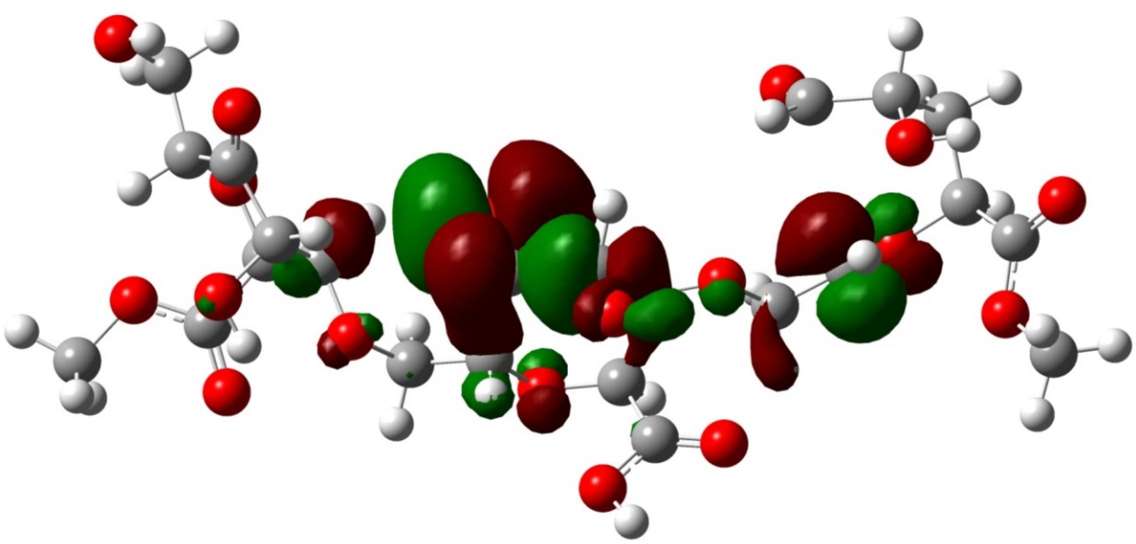

Figure 8. The highest occupied molecular orbital (HOMO) of Pectin using DFT at the B3LYP/6-31G(d) basic set in aqueous phase.

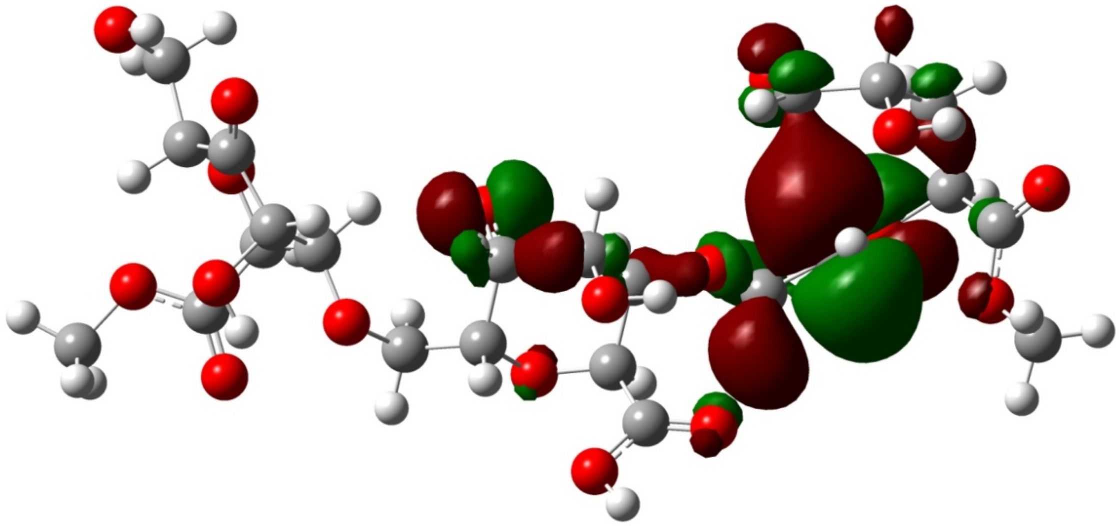

Figure 9.The lowest unoccupied molecular orbital (LUMO) of Pectin using DFT at the B3LYP/6-31G(d) basic set in aqueous phase.

CONCLUSIONS

Nopal extract act as a good corrosion inhibitor for mild steel in 1M HCl solution. The inhibition efficiency increased with increasing temperature. The change in free energy carries negative values around -20kJ/mole which indicate that the adsorption process is spontaneous and physical adsorption. The inhibitor efficiency increased with concentration of Nopal extract (except at 25ºC). The increase in *Rct* values and decrease in *Cdl* values confirm the formation of an insulated protective layer over the mild steel surface, which was supported by SEM images. The Computational Calculations of the chemical parameter such as HOMO, LUMO, hardness, fraction of electron transferred, etc were correlated with the inhibition efficiencies of the Pectin molecule.

ACKNOWLEDGEMENTS
Authors are highly thankful to Linda Landeros Martínez, Kathí Alejandra Ramirez Balderrama, Adan Borunda Terrazas, Jair Marcelo Lugo Cuevas, Gregorio Vazquez Olvera, Victor Manuel Orozco Carmona, Karla Campos Venegas, Luis de la Torre Saenz and Manuel Roman Aguirre for their generous assistance in this work.

REFERENCES

1. R.A. Prabhu, T.V. Venkatesha, A.V. Shanbhag, G.M. Kulkarni, R.G. Kalkhambkar. "Inhibition effects of some *Schiff´s* bases on the corrosion of mild steel in hydrochloric acid solution" Corrosion Science 50 (2008) 3356-3362.

2. J.P. Flores De los Ríos, M. Sánchez Carrillo, C.G. Nava Dino, J.G. Chacón Nava, J.G. González Rodríguez, E. Huape Padilla, M.A. Neri Flores, A. Martínez Villafañe. "*Opuntia ficus-indica* Extract as Green Corrosion Inhibitor for Carbon Steel in 1M HCl Solution" Journal of Spectroscopy 1(2015) 1-9.

3. M.A. Chidiebere, C.E. Ogukwe, K.L. Oguzie, C.N. Eneh, E.E. Oguzie. "Corrosion inhibition and adsorption behavior of *Punica granatum* extract on mild steel in acidic enviroments: Experimental and theoretical studies" Industrial & Engineering Chemistry Reserch. 51 (2012) 668-677.

4. J. Bhawsar, P.K. Jain, P. Jain. "Experimental and computational studies of *Nicotina tabacum* leaves extract as green corrosion inhibitor for mild steel in acidic medium" Alexandria Engineering Journal. 54 (2015) 769-775.

5. E. Rodriguez, J.G. Gonzalez, G. Valladarez, G.F. Dominguez. "Corrosion Inhibition of Carbon Steel in H_2SO_4 By *Chenopodium Ambrosioides*" International Journal of Electrochemical Science, 6 (2011) 6360-6372.

6. S. Umoren, I.B. Obot, Z. Gasem and N.A. Odewunmi. "Experimental and Theoretical Studies of Red Apple Fruit Extract as Green Corrosion Inhibitor for Mild Steel in HCl Solution" Journal of Dispersion Science and Technology, 36 (2015) 789-802.

7. S. Deng and X. Li. "Inhibition by *Ginkgo* leaves extract of the corrosion of steel in HCl and H_2SO_4 solutions" Corrosion Science. 55 (2012) 407-415.

8. A.M. Al Turkustani, S.T. Arab, L.S.S. Al Qarni. "*Medicago Sative* plant as safe inhibitor on the corrosion of steel in 2.0 M H_2SO_4 solution" Journal of Saudi Chemical. 15 (2011) 73-82.

9. M.A. Quraishi, Ambrish Singh, Vinod Kumar Singh, Dileep Kumar Yadav, Ashish Kumar Singh. "Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murraya koenigii* leaves" Materials Chemistry and Physics. 122 (2010) 114-122.

10. C. Kamal, M.G. Sethuraman. "*Spirulina platensis* A novel green inhibitor for acid corrosion of mild steel" Arabian Journal of Chemistry. 5 (2012) 155-161.

11. M.D. Leo, M. Brazual, A.M. Pawlowska, P.L. Cioni, A. Braca "Profiling the chemical content of Opuntia ficus-indica flowers by HPLC-PDA-ESI-MS and GC/EIMS analyses" 3 (2010) 48-52.

12. L.M. Rodríguez, A. Martínez, D. Glossman "Computational simulation of the molecular structure and properties of hererocyclic organic compounds with possible corrosion inhibition properties" Journal of Molecular Structure. 713 (2005) 65-70.

13. N.O. Obi, I.B. Obot, M.I. El, S.A. Unmoren, E.E. Ebeso "Computational Simulation and Statistical Analysis on the Relationship Between Corrosion Inhibition Efficiency and Molecular Structure of Some Phenanthroline Derivatives on Mild Steel Surface" International Journal of Electrochemical Science. 6 (2011) 5649-5675.

14. H. Chermette "Chemical reactivity indexes in density functional theory" Journal of Computational Chemistry. 20 (1999) 129-154.

15. R.G. Parr, P.K. Chattaraj, "Principles of maximum hardness" Journal Chemistry Society. 113 (1991) 1854-1855.

16. M.J. Dewar, W. Thiel, "Ground states of molecules 59 MNDO study of SN_2 reactions and related processes" Journal of American Chemical Society. 85 (1963) 3533.