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Corrosion Inhibition of Mild Steel using *Agavoideae* Extract in1M HCl Solution

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The effect of *Agaviodeae* (Agave) as green corrosion inhibitor for mild steel in HCl 1M solution has been investigated by weight loss measurements, potentiodynamic polarization curves and electrochemical impedance spectroscopy. Also, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) were applied. Various inhibitor concentrations were used in the range of 0 to 300 ppm at 298, 313 and 333 K. The results indicated that the inhibition efficiency increased with increasing *Agaviodeae* extract concentration, however, the inhibition efficiency decreased with increasing temperature. The inhibitor was found to behave as a mixed-type inhibitor. The inhibition behavior has been associated with adsorption effects. In fact, the adsorption of the inhibitor on the steel surface follows the Langmuir adsorption isotherm, indicating monolayer adsorption. On the whole, the highest efficiency (96%) was obtained at 300 ppm and 298 K.

Keywords: Mild steel, Corrosion inhibition, Adsorption.

1. INTRODUCTION

Acid solutions are often used in industry for cleaning, decaling and pickling of steel structures, processes which are normally accompanied by considerable dissolution of the metal. Corrosion of metals, however, is considered to be a serious problem in most industries. The new generation of environmental regulation requires the replacement of toxic inhibitors with non-toxic inhibitors. In this context, many alternative eco-friendly corrosion inhibitors have now been developed. A number of organic compounds are known to be applicable as corrosion inhibitors for steel in acidic environments. 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 *Brugmansia-suaveoles* and *Cassia-roxburghii*[1], *Musa-paradisica*[2], *Zenthoxylum-alatum*[3], *Spirulina-platensis*[4], *Olea-europaea*[5], *Punica-granatum*[6], *Lupinous-albus*[7], *Occimum-viridis*, *Telferia-occidentalis*, *Azadirachta-indica* and *Hibiscus-sabdariffa*[8], *Murraya-koenigii*[9], *Medicago-sative*[10], *Areca-catechu*[11], *Rosmarinus-officinalis*[12], *Ilex-paraguariensis*[13], Gundelia-tournefortii[14]. A number of organic compounds represent this type of inhibition, particularly those containing elements of Group V and VI of the periodic table, such nitrogen, phosphorous, arsenic, sulphur, oxygen and selenium. The efficiency of an organic compound as an inhibitor is mainly dependent upon its ability to get adsorbed on a metal surface[15]. It can then retard the cathodic and/or anodic reaction, thus, reducing the corrosion rate[16]. The stability of the adsorbed inhibitor film on the metal surface depend on some physicochemical properties of the molecule related to their functional groups, aromaticity, the possible steric effects, electronic density of donor atoms, type of corrosive environment and the nature of the interaction between the π orbital of the inhibitors and the d orbitals of iron[17,18]. This study aimed at investigating the inhibition effect of *Agaviodeae* extract on mild steel in 1M HCl solution using weight loss measurements and electrochemical techniques. The inhibitor was investigated and characterized using FT-IR, SEM and thermodynamic analysis.

2. EXPERIMENTAL

2.1. Preparation of specimens

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, 260, 400, 600 and 800 grade; and then thoroughly cleansed with distilled water and then with ethanol, being dried later on and kept in a desiccator till their use. While coupons of size 0.7850 cm^2 were used for electrochemical studies. It was encapsulated in commercial epoxy resin.

2.2. Inhibitor preparation

50 g of *Agavoideae* 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. The extract solid was prepared in a methanol solution 5% by weight.

2.3. Solution preparation

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

2.4. 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 300 ppm) for time of exposition of 4.5, 6.5, 12, 24, 48 and 120 hours. Times were based on related literature, showing the time period of action of the inhibitor. 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 298, 313 and 333 K by using a hot plate. Corrosion rates, in terms of weight loss measurements, ΔW, were calculated as follows:

$$\Delta W = (m_1 - m_2) / \mathrm{A} \tag{1}$$

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:

$$\mathrm{IE}\ (\%) = 100\ (\Delta W_1 - \Delta W_2) / \Delta W_1 \tag{2}$$

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

2.5. 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 (298, 313 and 333 K) and naturally aerated conditions. Polarization curves were recorder at a constant sweep rate of 1 mV/S at the interval from -500 to +500 mV respect to the E_{corr} value. The polarization curves were studied in 50 ml 1M HCl solutions using Potentiostat / Galvanostat Autolab-84861. The values of inhibition efficiency (%) were determined from equation (3), where, $Icorr_1$ and $Icorr_2$ are current densities with and without addition of inhibitor.

$$\mathrm{IE}\ (\%) = 100\ (Icorr_2 - Icorr_1) / Icorr_2 \tag{3}$$

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 electrical equivalent circuit for the system is shown in Figure 1. The impedance studies were studied using Solartron Impendace / Gain-Phase analyzer SI 1260. The corrosion inhibition efficiency (%) was determined by equation (4), where Rct_1 and Rct_2 are the charge transfer resistances in presence and absence of inhibitor.

$$IE\ (\%) = 100\ (Rct_2 - Rct_1) / Rct_2 \quad (4)$$

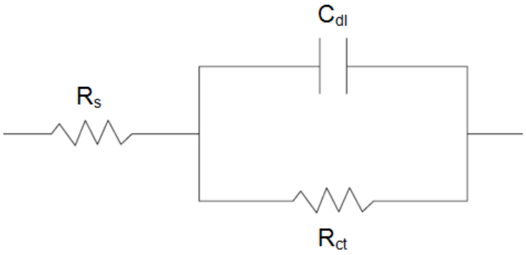

Figure 1. The equivalent circuit model for electrochemical impedance measurements.

2.6. 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 *Agavoideae* extract in 1M HCl and specimen. The immersed was for 24 hours in 298 K. After solvent evaporation, the surface film was scraped carefully and its FT-IR spectra were recorded using Perkin Elmer model spectroscopy.

2.7. Scanning electron microscope studies

Mild steel specimens were immersed in a corrosive environment of 1M HCl having an optimum concentration (300 ppm) of the *Agavoideae* extract for 24 hours at 298 K. 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.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Figure 2 shows the effect of inhibitor concentration on the inhibitor efficiency at the different tested temperatures. It can be seen that the inhibitor efficiency increased to a maximum value at 300 ppm as the inhibitor concentration was increased[19]. The increase in inhibitor efficiency is due to the increase in the number of constituent molecules of *Agavoideae* extract adsorbed on the metal surface at higher concentrations, so that the active sites of the metal are protected by inhibitor molecules.

Therefore, the efficiency was found to decrease with increasing the temperature. This behavior indicates desorption of the inhibitor molecule from the metal surface due to the decrease in the strength of the adsorption process.

Table 1 shows the values of inhibition efficiencies at different temperatures, indicating that inhibition efficiency decreased at higher temperatures.

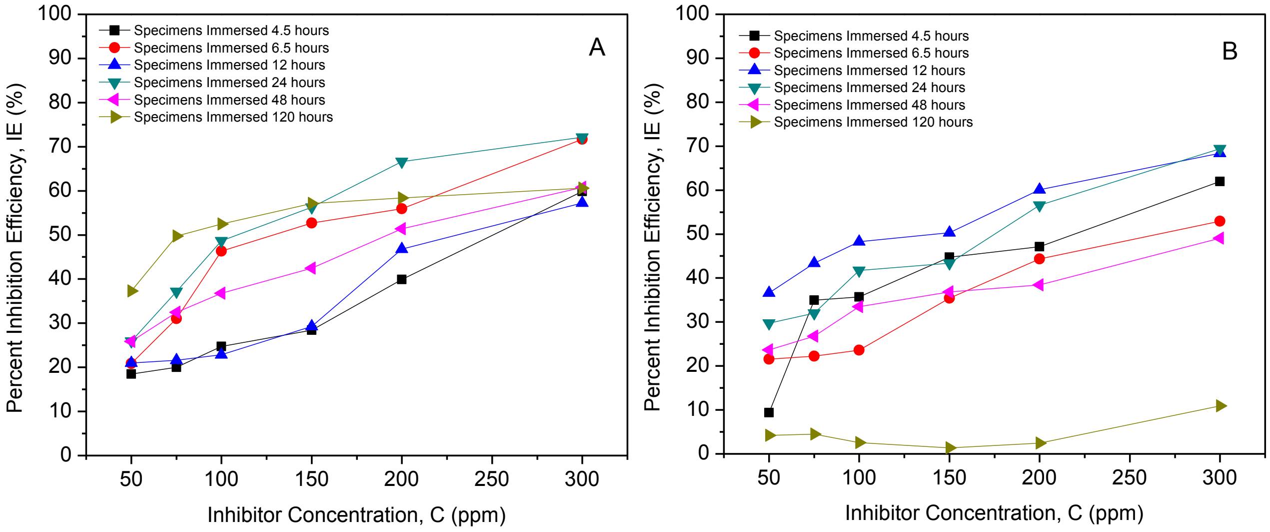

Figure 2. Inhibition efficiency of mild steel specimens at different immersed times in 1M HCl with *Agavoideae* extract using on the weight loss methods. A is 298 K and B is 313 K.

Table 1. Values of Inhibition Efficiency (%) from weight loss measurement for mild steel corrosion in 1M HCl with and without addition of different concentrations of *Agavoideae* extract at different temperatures.

Inhibitor Concentration (ppm)	Temperature (K)	Inhibition Efficiency (%)
0	298	---
50		21
75		31
100		46
150		53
200		56
300		72
0	313	---
50		29
75		32
100		41
150		43
200		56
300		69

3.2. Polarization measurements

Polarization curves for mild steel at various concentration of *Agavoideae* extract in 1M HCl at 298 K are shown in Figure 3. The corrosion current density (*Icorr*), corrosion potential (*Ecorr*), and cathodic and anodic Tafel slopes (*bc* and *ba)* were obtained by extrapolation of the anodic and cathodic regions of the Tafel plot.

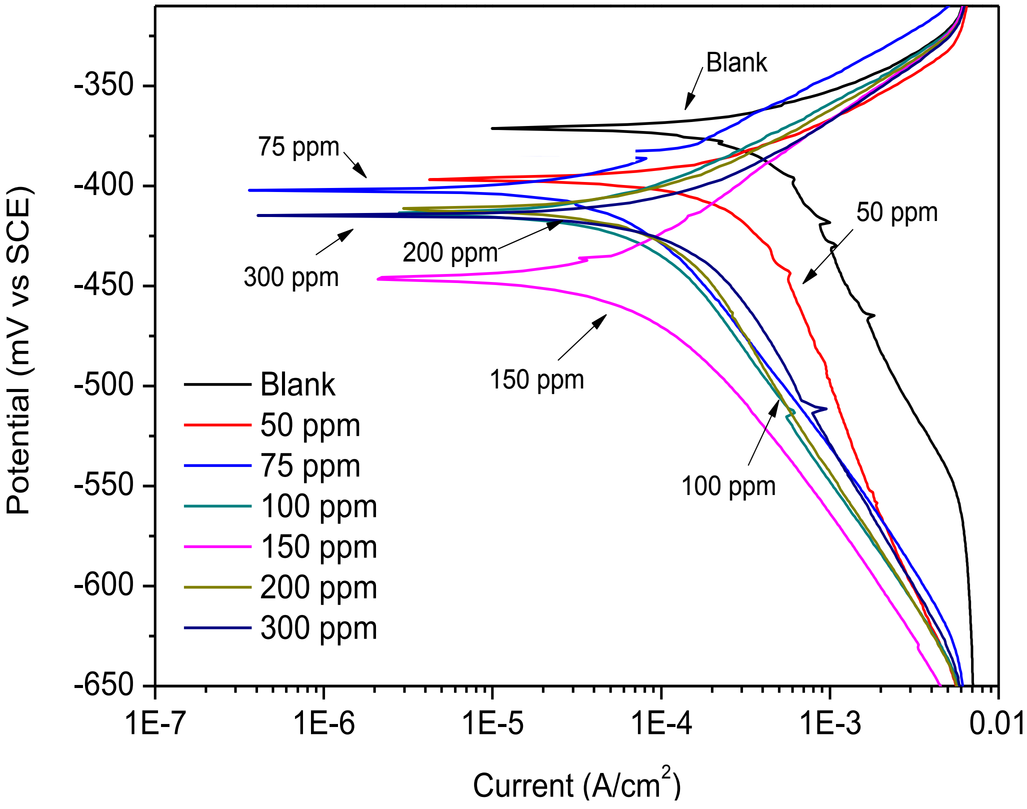

Figure 3. Polarization plots of mild steel obtained in 1M HCl solution at 298 K in absence and presence of various concentrations of *Agavoideae* extract.

Table 2. Determination of the electrochemical parameter for mild steel from polarization measurements.

Concentration (ppm)	**Temperature (K)**	**Ecorr (mVvs. SCE)**	**Icorr (µA/cm^2)**	**Bc (v/Dec)**	**Ba (v/Dec)**	**CR (mm/year)**	**IE (%)**
---	298	-384	601.5	46.4	171.4	6.98	---
50		-441	448.2	58.2	213.9	5.20	26
75		-419	242.6	62.9	153.7	2.81	60
100		-393	197.4	61.8	149.8	2.29	67
150		-410	148.9	52.5	139.2	1.73	75
200		-419	132.7	54.2	133.1	1.54	78
300		-440	106.1	81.1	106.3	1.23	82

The IE (%) was calculated using the equation 3. The electrochemical parameters obtained from the polarization measurements are listed in Table 2. As can be seen in Figure 3, the addition of *Agavoideae* extract to the corrosive solution reduces the anodic dissolution of iron and also retards the cathodic hydrogen evolution reactions as would be expected. Both corrosion current density and corrosion rate were considerably reduced in the presence of the extract. These results are indicative of the adsorption of inhibitor molecules on the mild steel surface. The inhibition of both anodic and cathodic reactions is increasingly pronounced when increasing *Agavoideae* extract concentration. These results suggest that *Agavoideae* extract can be classified as the mixed type corrosion inhibitor[20-22]. The highest inhibitor efficiency (82 %) was obtained by adding 300 ppm of extract.

3.3. Electrochemical impedance spectroscopy measurements

Figure 4 shows the representative Nyquist plots of mild steel obtained in 1M HCl solution in the absence and presence of various concentrations of *Agavoideae* extract. The Nyquist plot of mild steel obtained in blank solution was magnified and added in Figure 4. The Nyquist plots of mild steel showed a depressed semi-circular shape.

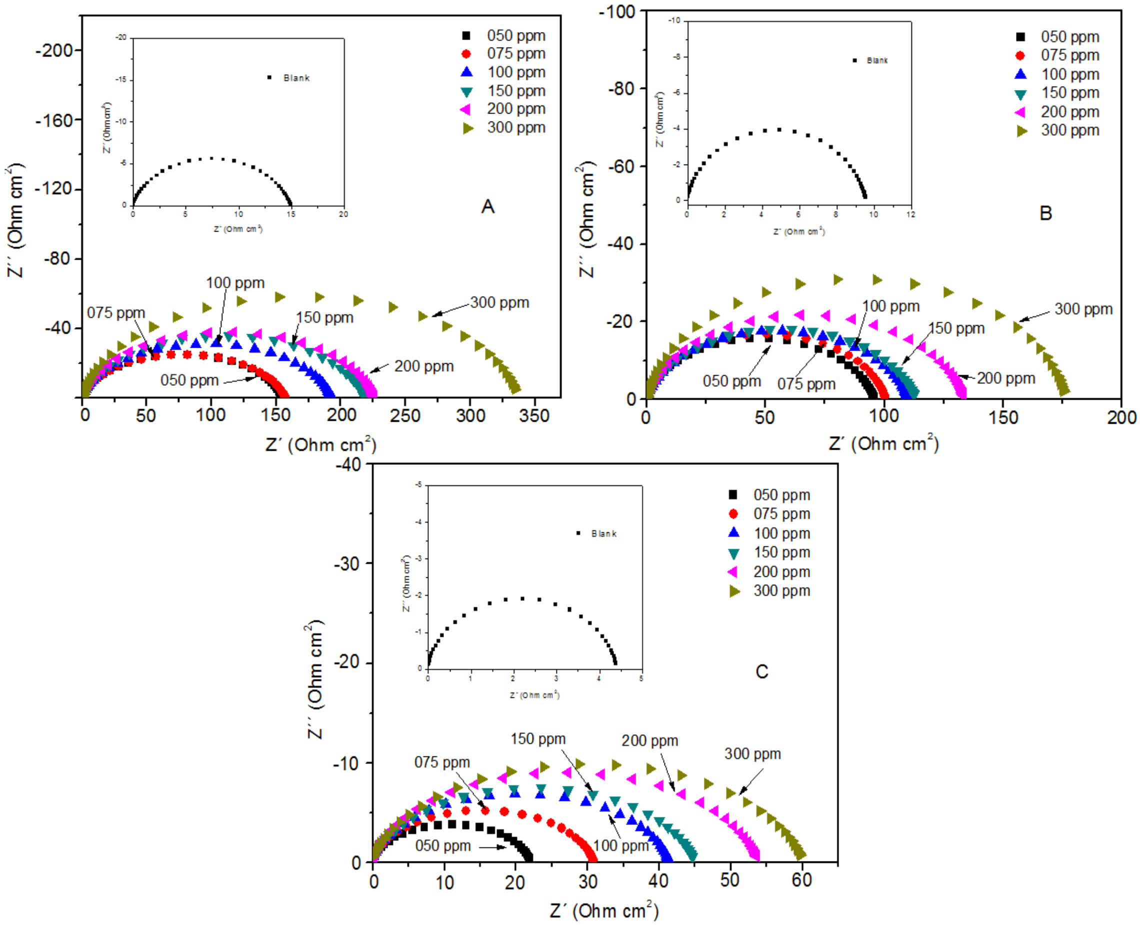

Figure 4. Nyquist plots of mild steel obtained in 1M HCl solution in the absence and presence of various concentrations of *Agavoideae* extract: A) 298 K, B) 313 K and C) 333 K.

This behavior indicates that the corrosion of mild steel in 1M HCl solution was mainly controlled by a charge transfer process. Although the appearance of Nyquist plots remained the same, their diameter increased after the addition of *Agavoideae* extract. This increase was also pronounced with increasing inhibitor concentration which indicates the adsorption of molecules on the metal surface[23,24]. The impedance parameters derived from the Nyquist plots and percentage inhibition efficiency are given in Table 3. Likewise it shows that the *Rct* values increased[25] 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[26,27]. To obtain the double layer capacitance (*Cdl*) values, the following equation was used:

$$Cdl = 1 / 2\pi f_{max} Rct \qquad (5)$$

The inhibition efficiency was calculated using the equation 4. The highest inhibitor efficiency (96 %) was obtained by adding 300 ppm of *Agavoideae* extract.

Table 3. Electrochemical impedance parameter values for the corrosion of mild steel in 1M HCl at different temperatures in the absence and presence of *Agavoideae* extract.

Temperature (K)	**Concentration (ppm)**	**Rct (Ω cm^2)**	**Cdl (μF cm^{-2})**	**Inhibition Efficiency (%)**
298	---	15.0	1061.0	---
	50	150.2	105.9	90
	75	152.4	104.4	90
	100	183.7	86.6	92
	150	218.4	72.9	93
	200	225.8	70.5	94
	300	333.7	47.7	96
313	---	9.5	1675.3	---
	50	97.2	163.7	90
	75	100.1	158.9	91
	100	115.3	138.0	92
	150	117.2	135.8	92
	200	132.4	120.2	93
	300	176.2	90.3	94
333	---	4.4	3617.2	---
	50	22.6	704.2	81
	75	31.5	505.3	86
	100	42.4	375.4	89
	150	45.1	352.9	90
	200	54.6	291.5	91
	300	60.2	264.4	92

3.4. Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 5 shows the FT-IR spectrum of the extracts at different concentrations. A careful investigation of the spectra revealed that all the extract showed almost similar peaks; however, the intensities decreased or increased with addition of the *Agavoideae* extract. A strong and broad peak at 3000/3300 cm^{-1} can be attributed to N-H stretching vibration. A small peak at 2900 cm^{-1} was observed for pure extract and before the test. Such a peak may be attributed to C-H stretching vibration; mean while a band was observed at 1420 cm^{-1} for pure extract and after the test due to C-C bending vibration. The absorptions bands at 1590/1600/1616 cm^{-1} were also observed due to a C=O or N=O stretching vibration, C=N stretching vibration and C=C stretching vibration respectively. A peak at 1400 cm^{-1} was attributed to C-N bending vibration before test. Peaks decreased before and after testing. However, peaks were increased for pure extract and assigned to C-N bending vibration at 1000 cm^{-1}. A peak at 700/800 cm^{-1} corresponds to N-H bending vibration for three tests. Thus, results showed that *Agavoideae* 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 4.

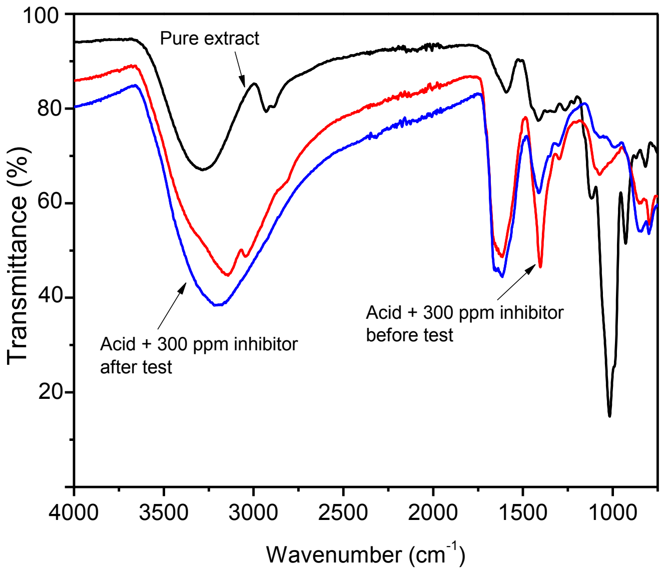

Figure 5. FT-IR spectrum of *Agavoideae* extract pure, before and after corrosion test.

Table 4. Peaks from FT-IR spectra of *Agavoideae* extract pure, before and after corrosion test, and their identification.

Pure extract		Acid + 300 ppm inhibitor before test		Acid + 300 ppm inhibitor after test	
Frequency (cm^{-1})	**Functional group and vibration type**	**Frequency (cm^{-1})**	**Functional group and vibration type**	**Frequency (cm^{-1})**	**Functional group and vibration type**
3300	N-H stretch	3300	N-H stretch	---	---
---	---	3200	N-H stretch	3200	N-H stretch
---	---	3000	N-H stretch	---	---
2900	C-H stretch	2900	C-H stretch	1667	C=O stretch
1590	C=O, N=O stretch	1616	C=C stretch	1600	C=N stretch
1420	C-C bending	1400	C-N bending	1420	C-C bending
1000	C-N bending	1000	C-N bending	1000	C-N bending
800	N-H bending	700	N-H bending	780	N-H bending

3.5 Adsorption Behavior

To investigate adsorption behavior of *Agavoideae* extract in 1M HCl solution, numerous isotherm models were employed, such as, Langmuir, Freundlich, Flory-Huggins, Frumkin, and Temkin, but the best fit was obtained for the Langmuir isotherm model. The Langmuir adsorption could be represented by the following equation:

$$C / \theta = (1 / K) + C \tag{6}$$

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:

$$\theta = IE\ (\%) / 100 \tag{7}$$

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior[28,29,30]. Basic information on the interaction between the inhibitor and the metal surface can be provided by an adsorption isotherm. 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 6 shows the Langmuir isotherm of the EIS method.

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:

$$\Delta G = -RTln(55.5K) \tag{8}$$

Where 55.5 is the water concentration of solution in mol / L. R is the ideal gas constant, T is the absolute temperature. Table 5 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). Their mechanism can be classified as mixed-type inhibitor[31,32].

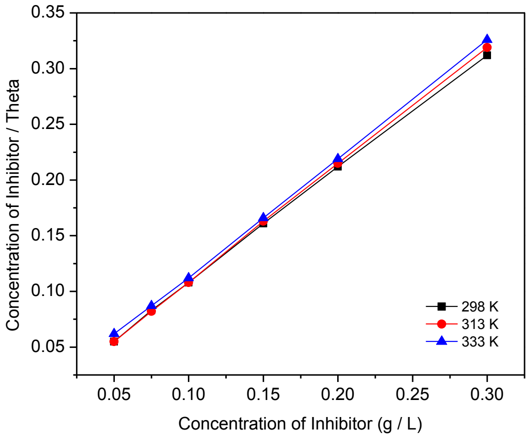

Figure 6. Langmuir isotherm for adsorption of *Agavoideae* extract on the mild steel surface. Electrochemical impedance spectroscopy data.

Table 5. Thermodynamic parameters for mild steel in 1M HCl in presence of the *Agavoideae* extract at different concentrations.

Method	Temperature (K)	Regression coefficient (R^2)	Slope	Adsorption constant (K)	Free energy of adsorption (ΔG)
EIS	298	0.99974	1.02634	182.149	-22.847
	313	0.99987	1.05705	350.877	-25.703
	333	0.99987	1.05937	133.155	-24.663

3.2 SEM images

The scanning electron microscope images were recorded to establish the interaction of inhibitor with the metal surface. Figure 7A indicates the finely polished characteristic surface of mild steel. Figure 7B revealed that the surface was severely corroded due to the aggressive attack by 1M HCl. Figure 7C reveal the formation of a protective film by the inhibitor on the mild steel surface in acid medium[33,34,35]. Images 7B and 7C show specimens immersed 24 hours at 298 K. The image 3C containing 300 ppm of *Agavoideae* extract in 1M HCl.

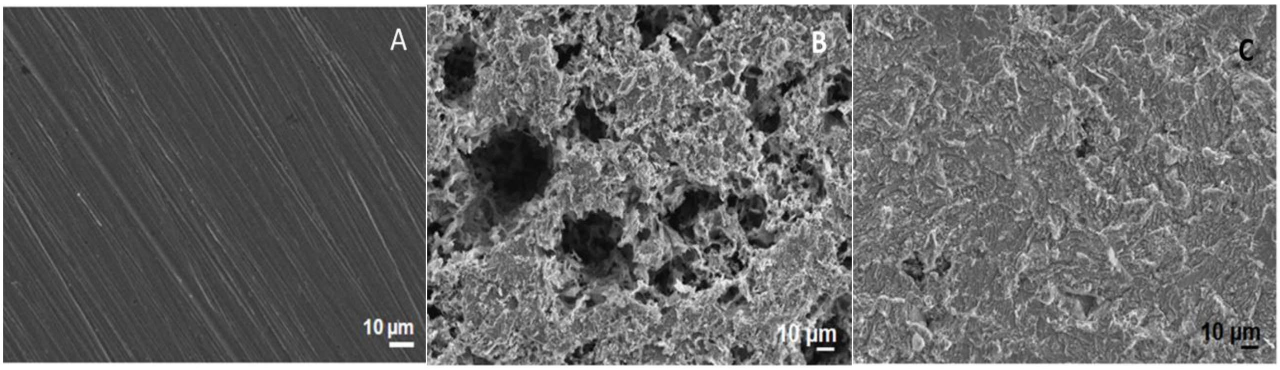

Figure 7. SEM images of (A) polished mild steel specimens. (B) mild steel specimens in HCl 1M. (C) mild steel specimens with *Agavoideae* extract in HCl 1M at 298 K.

4. CONCLUSIONS

Agavoideae extract act as a good corrosion inhibitor for mild steel in 1M HCl solution. The inhibition efficiency decreased 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, respectively. The inhibitor efficiency increased with concentration of *Agavoideae* extract. The inhibitor altered both anodic and cathodic Tafel slopes, which showed the mixed mode of action of the inhibitor molecule. 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 corrosion inhibitive effect shown by *Agavoideae* extract can be correlated to the presence of organic compounds in its chemical structure.

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