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# Electrochemical Studies on the Inhibition behavior of Aluminum in HCl Solution using Ziziphus Spina Christi Extract

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**ABSTRACT**

Ziziphus Spina Christi Extract (ZSCE) was tested as corrosion inhibitor for aluminum in 0.5 M HCl using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) measurements. Surface morphology was tested using scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX). The effect of temperature on the corrosion behavior of Al in 0.5 M HCl with and without different concentrations of plant extract was studied at temperatures of 298 and 318 K. Inhibition efficiency of 85.7% was achieved with 500 ppm ZSCE at 298 K. It is evident from the results obtained that ZSCE inhibits the corrosion in 0.5 M HCl through adsorption process following Langmuir adsorption isotherm. The inhibition efficiency increased with increase in extract concentration but decreased with raising temperatures. The mixed mode of action exhibited by the extract was confirmed by the polarization studies while SEM analysis substantiated the formation of protective layer over the Al surface. The values of inhibition efficiency obtained from different techniques are in good agreement.

## Introduction

Corrosion of aluminum and its alloys has been a subject of numerous studies due to high technological value and wide range of industrial applications especially in aerospace and house-hold industries. Aluminum and its alloys, however, are reactive materials and are prone to corrosion. A strong adherent and continuous passive oxide film is developed on Al upon exposure to aqueous solutions. This surface film is amphoteric and dissolves when the metal is exposed to high concentrations acids or bases [1]. Adsorption of organic compounds at the metal by forming a protective layer on the metal surface reduces the corrosion. The nature of the metal surface and the type of corrosive media determine the extent of adsorption [2]. A number of organic compounds [3-10] are known to be applicable as corrosion inhibitors for aluminum alloy in acidic environments. Such compounds typically contain nitrogen, oxygen or sulphur in conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier to corroded attack. The adsorption bond strength is dependent on the composition of the metal, inhibitor structure and concentration as well as temperature [9]. Despite the broad spectrum of organic compounds, the choice of appropriate inhibitor for a particular application is restricted by several factors. These include increased environmental awareness and the need to promote environmentally friendly process. Many previous studies showed that the naturally occurring substances of plant are successfully used as inhibitors for corrosion [11-13]. The natural products of plant origin are inexpensive, ecofriendly corrosion inhibitors. The extracts from their leaves, barks, seeds, and roots compose of mixture of organic compounds and some have been reported as effective inhibitors for metals and alloys corrosion in different aggressive environments [14-20]. In recent years, several green inhibitors have been used for the prevention of corrosion by most of the investigators. Few examples are *Parthenium hysterophorus* [21], *Punica granatum* [22], Asafoetida Extract [23], Red Peanut Skin [24], *Eupatorium Odoratus* [25], Rice Husk Ash [26], *Achyranthes aspera* [27], *Citrulus vulgaris* peel [28], *Albizia lebbeck* seed [29], *Hibiscus esculenta* leaves [30], *Jatropha curcas* [31], *Polyalthia Longifolia* [32].

Thus in our present study, the inhibitive and adsorption properties of ZSCE on the corrosion of Al in presence and absence of various concentration of ZSCE extract have been investigated at 298 K by the chemical and electrochemical techniques and the corrosion product on metal surface is analyzed by SEM and EDX.

## Experimental

### *Materials and solutions*

Corrosion tests have been carried out on electrodes cut from sheets of aluminum with composition (weight %):

The corrosive medium (0.5 M HCl) was prepared from a stock 5 M HCl solution by dilution with bi-distilled water from the concentrated acid solution (37 %, Merck). The concentration of the stock acid solution was checked by standard solution of $Na_2CO_3$. This solution was used as a blank

### *Ziziphus Spina Christi extract solutions*

The Ziziphus Spina Christi extract was obtained directly from the powder of dried leaves of Ziziphus Spina Christi. Ziziphus Spina Christi were soaked in methanol and left standing for 7 days. The solution was filtered and further distilled at 40°C to remove the methanol from the Ziziphus Spina Christi solution extracts and then concentrated to dryness.

### *Chemical composition of Ziziphus Spina Christi extract*

The plant has been extensively studied [33] and its chemical composition is well-known [34, 35]. The main constituents of the essential oil were alpha-terpineol (16.4%) and linalool (11.5%). The main neutral hydrocarbons were n-pentacosane forms (81%). Methyl esters isolated from leaves included methyl

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palmitate, methyl stearate and methyl myristate. Beta-Sitosterol, oleanolic acid and maslinic acid were the main aglycones of the glycosides present in leaves.`Sugars present in leaves included lactose, glucose, galactose, arabinose, xylose and rhamnose. The plant also contains four saponin glycosides [36]. The highest flavonoid content was found in the leaves (0.66%). No significant influence of growing site or year of harvesting on the flavonoid content was observed. As quercetin 3-O-rhamnoglucoside 7-O-rhamnoside are the main flavonoid compounds present in all plant parts investigated [37]. The composition of the plant has always proved complex in its chemistry, also contain the known alkaloids, zizyphine-F, jubanine-A and amphibine-H.

### Weight Loss Measurements

The weight experiments were carried out using specimens of aluminum having dimensions (2 x 2 x 0.05 cm). The test pieces of Al samples were weight up to fourth decimal place using digital electronic balance. The test samples were immersed in 50 mL of 0.5 M HCl in absence and presence of varying concentration of Ziziphus Spina Christi extract taken in beaker at temperatures 25 and 45ºC. Initial weight of samples were measured before immersion and after specified period of exposed time, each piece was taken out of the test solution, rinsed with bi-distilled water, dried between two filter papers and weighed again. The difference in weight for an exposed period of 30-180 minutes was taken as the total weight loss. The experiments were carried out at various concentrations (100-500 ppm) of Ziziphus Spina Christi extract. Triplicate samples were used to check reproducibility of results. From the average weight loss results` the corrosion rate, the percentage of inhibition efficiency (%IE) and the degree of surface coverage (θ) were calculated using equation (2) [38]:

$$\text{Corrosion rate} = \Delta W/At \qquad (1)$$

where $\Delta W$ is the weight loss in mg, A is the area of the specimen in $cm^2$ and t is the exposure time in min.

where $W_2$and $W_1$are the weight losses for Al sample in the presence and absence of the inhibitor and θ is the degree of surface coverage of the inhibitor. The percentage of inhibition efficiency (% IE) and the degree of surface coverage (θ) were calculated from Eq. (2):

$$\text{Inhibition efficiency (\%IE)} = \Theta \times 100 = [(W_1-W_2)/W1] \times 100 \qquad (2)$$

### Electrochemical measurements

All electrochemical measurements (potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM)) were carried out using Gamry Potentiostat/Galvanostat/ZRA (model PCI4/300) with a Gamry framework system based on ESA400. Gamry applications include software DC105 for potentiodynamic polarization, EIS300 for EIS measurements and EFM140 for EFM measurements; computer was used for collecting data. Echem Analyst 5.5 Software was used for plotting, graphing and fitting data. All electrochemical measurements carried out using a conventional cell with three electrodes were used. The Al sheet was used as working electrode; the counter electrode was Pt wire electrode and the reference electrode is saturated calomel electrode (SCE). The working electrode was polished and cleaned as mentioned before.

### *Potentiodynamic polarization measurements*

For potentiodynamic polarization measurements, the three electrodes polarization cell was filled with 100 ml of test solution. The potentiodynamic current – potential curves were recorded by changing the electrode potential automatically from -0.8 V to 0.5 V at a scan rate of 1 $mVs^{-1}$. The degree of surface coverage (θ) and inhibition efficiency (%IE) were calculated using equation (3):

$$\% IE = \theta \times 100 = [1-(i/ i°)] \times 100 \qquad (3)$$

where i° and i are the current densities in the absence and presence of the extract, respectively.

### *Electrochemical impedance spectroscopy (EIS) measurements*

Electrochemical impedance spectroscopy is a powerful technique for the characterization of electrochemical systems and provides a wealth of kinetic and mechanistic information. For this reason this technique is being applied to an increasing extent to understand corrosion process in solution, to study rate determination, inhibitor performance, coating performance and passive layer characteristics [39-41].The electrochemical impedance measurements were carried out over a frequency range of $10^5$ Hz to 0.1 Hz with a signal amplitude perturbation of 10 mV. Experiments were always repeated at least three times. The impedance diagrams were given in Nyquist representations. In the represented electrical equivalent circuit (Figure 1), $R_s$ is the solution resistance, $R_{ct}$ is the charge transfer resistance and $C_{dl}$ is the double layer capacitance. The inhibition efficiency was calculated from the charge transfer resistance ($R_{ct}$) values using the following Equation (4):

$$\% IE= \Theta \times 100 = [(R^{\circ}_{ct} - R_{ct}) / R'ct] \times 100 \qquad (4)$$

where $R^o_{ct}$ and $R_{ct}$ are the charge transfer resistance in the absence and presence of inhibitor, respectively.

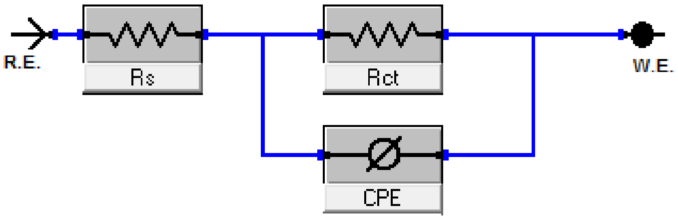

**Figure 1. Equivalent circuit proposed to fit the EIS experimental data**

### *Electrochemical frequency modulation (EFM) measurements*

The electrochemical frequency modulation (EFM) technique is a new tool for monitoring the electrochemical corrosion. The theory of EFM technique is previously reported [42]. The electrochemical frequency modulation has many features [43]. EFM is a non- destructive technique, rapid test, gives directly value of the corrosion current without a prior of knowledge of Tafel constants and has a great strength due to casually factors, which serve an internal check on the validity of the EFM measurement.

### *Scanning electron microscopy (SEM) studies*

A scanning electron microscope (SEM) model HITACHI S-3000H coupled to an analyzer EDAX –RONTEC, were used to analyze the morphology of the Al surface without and with the extract. Images of the samples were recorded after 24h exposure time in 0.5 M HCl without and with different concentration of Ziziphus Spina Christi extract. These samples underwent the same pre-treatment as those used in the experiments of weight loss and electrochemistry.

## Results and discussion

### Weight loss method

The weight loss of aluminum both in 0.5 M HCl in the absence and presence of various concentrations (100-500 ppm) of Ziziphus Spina Christi extract were determined. In all cases the weight loss decreases with increasing of extract. The experimental data of weight loss ($\Delta W$), percentage of inhibition efficiency (%IE), corrosion rate (C.R.) and degree of surface coverage ($\theta$) for aluminum in 0.5 M HCl and presence of various concentration of Ziziphus Spina Christi extract at different two temperatures are shown in Table 1. The corrosion rate values were plotted against the concentration of the extract in 0.5 M HCl Figure 2.

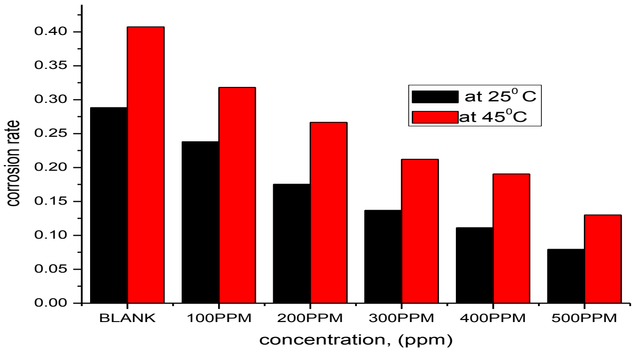

**Figure 2. Corrosion rates of Al in 0.5 M HCl at various concentrations of the extract at different temperatures**

The characterization of the corrosion of aluminum in the different corrosive solution will carried out by assessment of the inhibition efficiency (% IE) using equation 2. A bar chart of inhibition efficiency to concentration of inhibitor in 0.5 M HCl was plotted as shown in Figure 3.

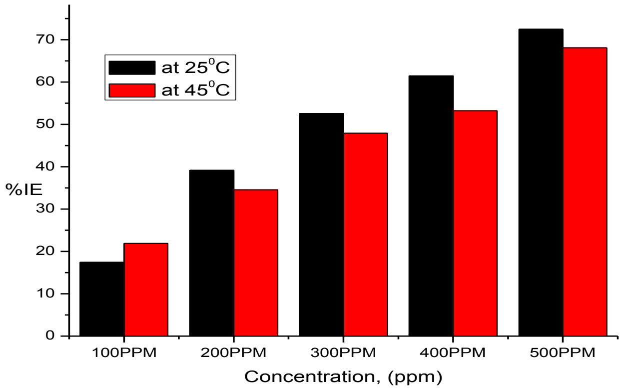

**Figure 3. Variation of inhibition efficiency of Al in 0.5 M HCl solutions with extract concentrations**

## Adsorption isotherms

Further elucidation of adsorption mechanism from the experimental data requires estimation of the adsorption modes of the inhibiting species whether (molecular or ionic). The predominant adsorption mode will be dependent on factors such as the extract composition, chemical changes to the extract and the nature of the surface charge on metal. To determine the adsorption mode, various isotherms were tested and curve fitting of corrosion data in 0.5 M HCl in presence of different concentrations of extract at 298 K. Figure 4 confirms that the inhibition process is due to adsorption of the Ziziphus Spina Christi extract on the metal surface. This is because a straight line is obtained when Log ($C/\theta$) is plotted against log C and the linear correlation coefficient of the fitted data is close to 1. This indicates that the adsorption of Ziziphus Spina Christi extract molecules obeys the Langmuir adsorption model [44] expressed as:

$C/\Theta = 1/K + C$ (5)

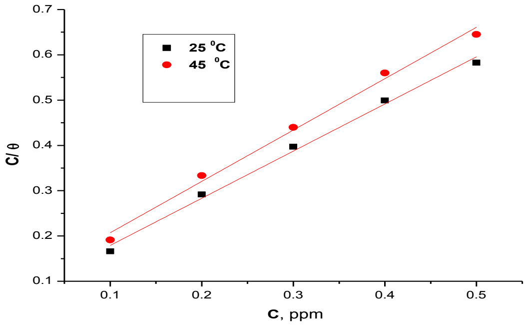

**Figure 4. Langmuir isotherm for Ziziphus Spina Christi adsorption on Al in 0.5 M HCl at two different temperature after 90 min. immersion.**

where C is the inhibitor concentration and $K_{ads}$ is the equilibrium constant for the adsorption /desorption process of the inhibitor molecules on the metal surface. The relationship between the equilibrium constant, $K_{ads}$, of adsorption and the free energy of adsorption, $\Delta G^{o}_{ads}$, is given by the following expression [45].

$\Delta G^{o}_{ads}=-2.303\ RT \log (55.5\ K)$ (6)

Values of free energy of adsorption calculated from equation 6 using $K_{ads}$ values obtained from Langmuir adsorption isotherm are presented in Table 2. The values are negative and less than -40 kJ $mol^{-1}$. This implies that the adsorption of the inhibitor on aluminum surface is spontaneous and confirms the physical adsorption isotherm mechanism [46]. A Plot of log $\theta/1-\theta$ against log C (Figure 5) at different concentrations of tested extract, straight lines were obtained indicating that adsorption follows kinetic thermodynamic model according Equation 7 [47]:

$\text{Log}\ \theta/1\text{-}\theta = \log (K') + y \log C$ (7)

The equilibrium constant of adsorption is $K_{ads} = K'^{(1/y)}$, where 1/y is -the number of surface active sites occupied by one inhibitor molecules and C is the bulk concentration of the inhibitor. The results are shown in Table (2). According to the data in this table, it is seen that the values of 1/y are nearly 1 indicating that each inhibitor molecule occupies one active site.

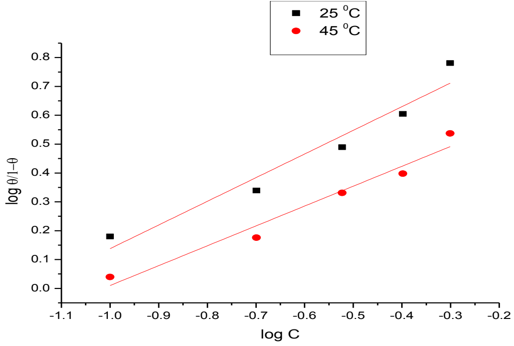

**Figure 5: The kinetic-thermodynamic model the adsorption of Ziziphus Spina Christi extract on aluminum surface at 298 K**

The corrosion data fit the first- order reaction rate law according to equation (8) [47]

$\text{Log}\ [Wi-\Delta W] = -\ kt/2.303+\text{LogWi}$ (8)

where Wi is the initial weight of aluminum specimen, $\Delta W$ is the weight loss of aluminum specimen at time t,[Wi-$\Delta W$] is the residual weight of aluminum coupon at time t and k is the first –order rate constant. The linear plots obtained with correlation coefficients close to 1 confirm first -order kinetics for the corrosion of aluminum in 0.5 M HCl solution in the presence and absence of Ziziphus Spina Christi extract Figure 6.

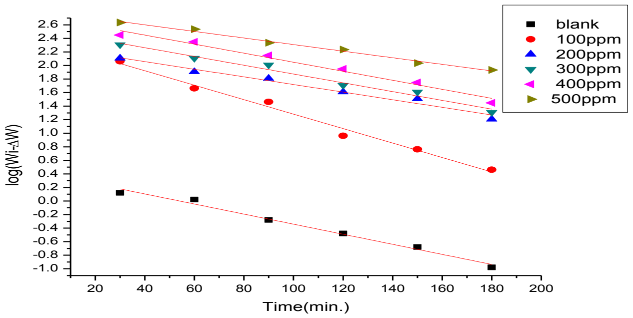

**Figure 6: Plot of log (Wi- ΔW) versus time for Al in 0.5 M HCl solution without and with Ziziphus Spina Christi extract**

## Effect of temperature

Two main types of interaction often describe adsorption of organic inhibitors on a corroding system viz: chemical adsorption and physical adsorption. It has been suggested [48] the physisorbed molecules are attached to the metal at the cathode and essentially retard metal dissolution by stifling the cathodic reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. The data reveal that the protection efficiency decreases with an increase in temperature. This can be due to the decrease in the strength of adsorption process at higher temperature, suggesting that physical adsorption of the extract components on the Al surface. The apparent activation energies ($E_a$) for the corrosion process in absence and presence of extract can be evaluated from Arrhenius equation (9):

$$\text{Log}\ (\text{C.R.})_2 / (\text{C.R.})_1 = E_a/2.303R \times (1/T_1 - 1/T_2) \qquad (9)$$

The heats of adsorption ($Q_{ads}$) can be obtained from the variation of surface coverage with temperature as follows [48]:

$$Q_{ads} = 2.303R\ [\log (\Theta_2/ 1-\Theta_2) - \log (\Theta_1/ 1-\Theta_1)] \times T_1T_2/T_2-T_1 \qquad (10)$$

### *Potentiodynamic polarization measurements*

Potentiodynamic polarization curves have been recorded for aluminum in 0.5 M HCl solution in different concentrations of Ziziphus Spina Christi extract at 25°C Figure 7. Electrochemical parameters extracted from polarization curves including corrosion potential ($E_{corr}$), corrosion current ($i_{corr}$), anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$) have been measured and by Tafel extrapolation and presented in Table 4. The results of this Table showed that this extract cause change in the anodic and cathodic Tafel slopes and no definite trend was observed in the shift of $E_{corr}$ values in the presence of different concentrations of the tested extract, suggesting that this extract behave as mixed-type inhibitor. Meaning that the addition of extract reduces the anodic dissolution of aluminum and also retards the cathodic reactions. The results obtained from the polarization technique were in good agreement with those obtained from the weight loss method.

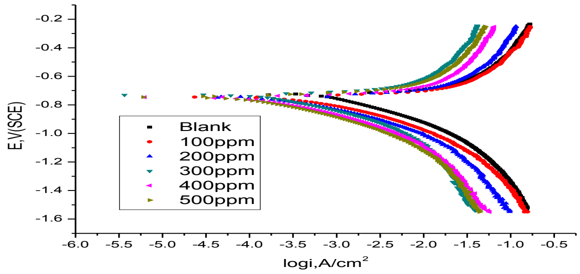

**Figure 7: Anodic and cathodic Tafel polarization curves for Al in the absence and presence of various concentrations of Ziziphus Spina Christi extract**

## Electrochemical impedance spectroscopy (EIS) measurements

EIS technique was applied to investigate the electrode /electrolyte interface and corrosion processes that occur on aluminum surface in the presence and absence of Ziziphus Spina Christi. To ensure complete characterization of the interface and surface processes, EIS measurements were made at OCP in a wide frequency range at 298 K The impedance spectra of aluminum in 0.5 M HCl solutions in the absence and presence of five different concentrations of Ziziphus Spina Christi were recorded. Figure 8 shows the impedance spectra in Nyquist format. The impedance diagrams display one single capacitive loop represented by slightly depressed semi-circle for the extract. This capacitive loop indicates that the corrosion of aluminum in 0.5 M HCl solution is mainly controlled by charge transfer process and formation of a protective layer on the metal surface. Deviations from the ideal semi-circle are generally attributed to the frequency dispersion as well as in homogeneities, roughness of metal surface and mass transport process [49-51]. The diameters of the capacitive loop obtained increases in the presence of extract, and were indicative of the degree of inhibition of the corrosion process. In addition to the high frequency capacitive loop, the semi-circles rolled over and extended to the fourth quadrant, and a pseudo-inductive loop at low frequency end was observed, indicating that Faradic process is taking place on the free electrode sites. This inductive loop is generally attributed to the adsorption of species resulting from the Al dissolution and the adsorption of hydrogen [52]. On the other hand, the similar nature of impedance diagrams obtained in the absence and presence of extract reveal that the addition of extract does not change the mechanism for the dissolution of aluminum in HCl [53]. The increase of $R_{ct}$ values with extract concentration may suggest the formation of a protective layer on the aluminum surface. This layer makes a barrier for mass and charge-transfer. The double layer capacitances ($C_{dl}$) were calculated using Eq. (11) [54].

$$C_{dl} = (2\pi f_{max} R_{ct})^{-1} \qquad (11)$$

where $f_{max}$ is the frequency value at which the imaginary component (Z”) of impedance is maximum. The data obtained from fitted spectra are listed in Table (5). By increasing the inhibitor concentration, the $R_{ct}$ values increase and the calculated $C_{dl}$ values decrease. The decrease in the $C_{dl}$, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that Ziziphus Spina Christi extract molecules function by adsorption at the metal/solution interface. The impedance data of the aluminum in the presence of different extract concentrations were analyzed using the equivalent circuit shown in Figure 1.

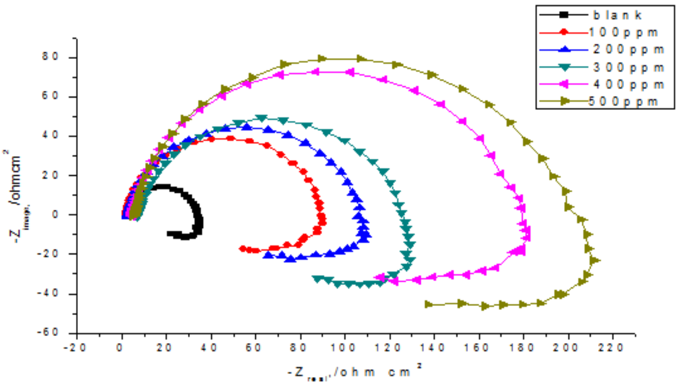

**Figure 8: Nyquist plots for aluminum in 0.5 M HCl in absence and presence of various concentrations of Ziziphus Spina Christi extract**

## Electrochemical frequency modulation (EMF) measurements

Electrochemical frequency modulation technique has many features, non-destructive technique, and rapid test, gives directly values of the corrosion current without a prior knowledge of Tafel constants and has great strength due to the causality factors, which serve as an internal check on the validity of the EFM measurements [38]. Like EIS, it is a small ac signal. Unlike EIS, however, two sine waves (at different frequencies) are applied to the cell simultaneously. Because current is a non-linear function of potential, the system responds in a nonlinear way to the potential excitation. The current response contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies. The two frequencies may not be chosen at random, they must both be small, integer multiples of a base frequency that determines the length of the experiment. Table (6) shows the corrosion kinetic parameters such as inhibition efficiency, corrosion current density (μA $cm^{-2}$), Tafel constants ($\beta_a$, $\beta_c$) and causality factors (CF-2, CF-3) at different concentrations of extract in 0.5 M HCl at $25^0$C. The causality factors in Table (6) indicate that the measured data are of good quality. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. If the causality factors differ significantly from the theoretical values of 2.0 and 3.0, then it can be deduced that the measurements are influenced by noise. If the causality factors are approximately equal to the predicted values of 2.0 and 3.0, there is a causal relationship between the perturbation signal and the response signal. Then the data are assumed to be reliable [56]. When CF-2 and CF-3 are in a range 0-2 and 0-3, respectively, then the EMF data is valid. From Table (6), the corrosion current densities decrease by increasing the concentrations of inhibitor. The inhibition efficiencies increase by increasing inhibitor concentrations. Inhibition efficiency ($\%IE_{EFM}$) depicted in Table 6 were calculated from the following equation 2.

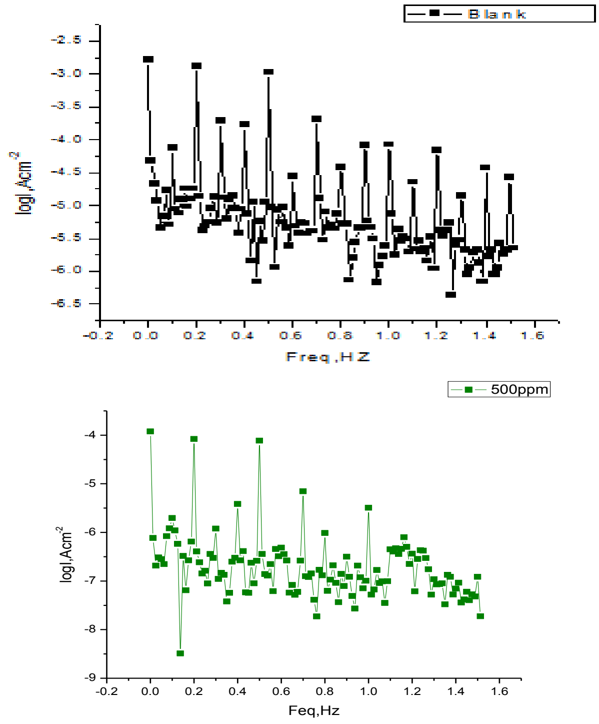

**Figure 9. Intermodulation spectra recorded for aluminum electrode in 0.5 M HCl solutions in the absence and presence various concentrations of Ziziphus Spina Christi extract**

## Surface morphology studies

Figure 10 shows the SEM photos of aluminum surface. It can be seen from Figure 10 (a) that the aluminum samples before immersion seems smooth and appears some abrading scratches on the surface. After immersion in uninhibited 0.5 M HCl solution for 24 h, the aluminum surface appears an aggressive attack of the corroding medium as shown in Figure 10(b). Furthermore, the corrosion products appear very uneven and cube-shaped morphology, and the surface layer is rather rough. By contrast, Figure 10(c) shows that there is much less damage on the aluminum surface in the presence of inhibitor, which further confirms the inhibition ability. Also, there might be an adsorbed film adsorbed on aluminum surface which does not exist in Figure 10(b). In accordance, it might be concluded that the adsorption film can efficiently retards the corrosion of aluminum.

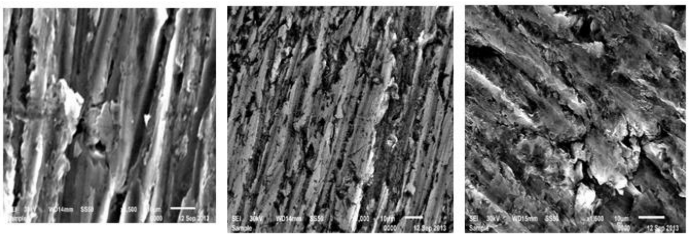

**Figure 10. Scanning electron microgram of polished aluminum (1500x) (a)alone(b) after exposure to 0.5 M HCl (c) after exposure to 0.5 M HCl containing 500 ppm of Ziziphus Spina Christi extract**

Figure 11 shows the EDX spectrum in the absence and presence of inhibitor figure show an additional line characteristic for the existence of O. in addition, the intensities of C signal are enhanced. The appearance of O signal and this enhancement in the C signal is due to the C and O atoms constituting the inhibitor. Which indicate that the inhibitor molecules have adsorbed on the metal surface. Data obtained from spectra are presented in Table 7. The spectra show also that Al peaks are considerably suppressed in the presence of inhibitor which is due to the overlying inhibitor film. These results confirm those from electrochemical measurements which suggest that a surface film inhibits the metal dissolution, and hence retard the hydrogen evolution reaction [57].

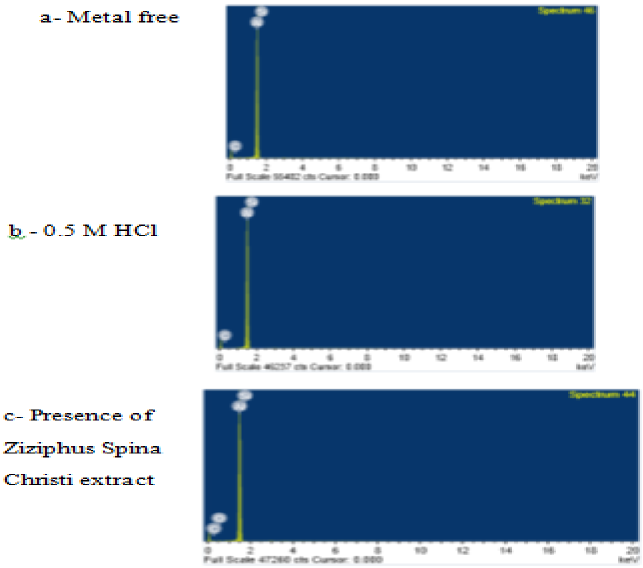

**Figure 11: EDX spectra of aluminum: (a) before of immersion in 0.5 M M HCl, (b) after 24 h of immersion in 0.5 M HCl and (c) after 24h of immersion in 0.5 M HCl + 500 ppm Ziziphus Spina Christi extract at 25 °C**

**Table 1. Data obtained from weight loss for Al corrosion in 0.5 M HCl at various concentrations of Ziziphus Spina Christi after 1.5 h at different temperatures**

| Concentration, ppm | 298 K | | | | 318K | | | |
|---|---|---|---|---|---|---|---|---|
| | ΔW | θ | %IE | CR, mg/cm$^2$h | ΔW | θ | %IE | CR, mg/cm$^2$h |
| Blank | 3.1 | ---- | ---- | 0.558 | 3.6 | ---- | ---- | 0.666 |
| 100 | 1.4 | 0.602 | 60.2 | 0.222 | 2.1 | 0.522 | 52.2 | 0.318 |
| 200 | 1.0 | 0.685 | 68.5 | 0.175 | 1.6 | 0.600 | 60.0 | 0.266 |
| 300 | 0.8 | 0.755 | 75.5 | 0.136 | 1.4 | 0.682 | 68.2 | 0.212 |
| 400 | 0.7 | 0.801 | 80.1 | 0.111 | 1.2 | 0.714 | 71.4 | 0.190 |
| 500 | 0.5 | 0.857 | 85.7 | 0.079 | 0.9 | 0.775 | 77.5 | 0.150 |

**Table 2. Langmuir, and Kinetic model of adsorption parameters for the adsorption of Ziziphus Spina Christi extract on aluminum surface in 0.5 M HCl after 90 min. immersion different temperatures**

| Temp. ºC | Langmuir isotherm | | | Kinetic model | | | |
|---|---|---|---|---|---|---|---|
| | $K_{ads}$ | $R^2$ | $-\Delta G^o_{ads}$ | 1/y | Log $K_{ads}$ | $R^2$ | $-\Delta G^o_{ads}$ |
| 25 | 13.3 | 0.99 | 16.34 | 1.2 | 1.17 | 0.93 | 16.59 |
| 45 | 10.68 | 0.99 | 16.89 | 1.4 | 1.01 | 0.95 | 16.77 |

**Table 3. Calculated values of apparent activation energy ($E_a$) and heat of adsorption ($Q_{ads}$) of extract on Al in 0.5 M HCl at different temperatures**

| Concentration ppm | $E^*$ kJ mol$^{-1}$ | $-Q_{ads}$ kJ mol$^{-1}$ |
|---|---|---|
| 0.5 M HCl | 7.0 | ----- |
| 100 | 14.2 | 12.8 |
| 200 | 16.5 | 14.6 |
| 300 | 17.5 | 14.3 |
| 400 | 21.2 | 18.8 |
| 500 | 25.3 | 21.8 |

**Table 4. Electrochemical kinetic parameters obtained by Tafel polarization technique for aluminum in absence and presence of various concentrations of Ziziphus Spina Christi extract**

| Concentration (ppm) | $-E_{corr}$ mV vs. SCE | $i_{corr}$ μA cm$^{-2}$ | $\beta_a$ mV dec$^{-1}$ | $-\beta_c$ mV dec$^{-1}$ | θ | % IE |
|---|---|---|---|---|---|---|
| Blank | 729 | 1990 | 147 | 293 | | |
| 100 | 746 | 916 | 121 | 255 | 0.540 | 54.0 |
| 200 | 748 | 619 | 119 | 257 | 0.689 | 68.9 |
| 300 | 730 | 421 | 120 | 260 | 0.788 | 78.8 |
| 400 | 748 | 381 | 125 | 277 | 0.808 | 80.8 |
| 500 | 745 | 304 | 149 | 278 | 0.847 | 84.7 |

**Table 5. EIS data for aluminum corrosion in 0.5 M HCl in the presence and absence of different concentrations of Ziziphus Spina Christi extract**

| Conc., ppm | $R^*_{ct}$ Ω cm$^{-2}$ | $R_{ct}$, Ω cm$^{-2}$ | Y° x 10$^6$ μΩ$^{-1}$s$^n$ | n | $C_{dl}$, μF cm$^2$ | θ | % IE |
|---|---|---|---|---|---|---|---|
| Blank | 2.69 | 28.35 | 79.3 | 0.921 | 47.0 | | |
| 100 | 2.02 | 75.84 | 82.52 | 0.948 | 62.4 | 0.626 | 62.6 |
| 200 | 2.68 | 92.04 | 65.09 | 0.929 | 44.0 | 0.692 | 69.2 |
| 300 | 6.95 | 108.70 | 48.17 | 0.904 | 27.6 | 0.739 | 73.9 |
| 400 | 4.60 | 154.80 | 43.52 | 0.927 | 29.4 | 0.816 | 81.6 |
| 500 | 5.11 | 180.8 | 46.70 | 0.911 | 29.2 | 0.843 | 84.3 |

**Table 6. Electrochemical kinetic parameters obtained by EFM technique for aluminum in 0.5 M HCl in the absence and presence of different concentrations of Ziziphus Spina Christi extract**

| Conc., ppm | $i_{corr}$ , μA cm$^{-2}$ | $\beta_a$, mV dec$^{-1}$ | $\beta_c$, mV dec$^{-1}$ | CF-2 | CF-3 | | % IE | |
|---|---|---|---|---|---|---|---|---|
| Blank | 984.4 | 142 | 175 | 1.6 | 2.5 | ------- | ------ | 593.20 |
| 100 | 327.4 | 100 | 150 | 2.0 | 2.9 | 0.670 | 67.0 | 197.20 |
| 200 | 287.0 | 101 | 151 | 1.6 | 2.8 | 0.708 | 70.8 | 172.90 |
| 300 | 207.5 | 49 | 157 | 1.5 | 2.5 | 0.789 | 78.9 | 125.00 |
| 400 | 139.8 | 96 | 138 | 1. 6 | 3.0 | 0.858 | 85.8 | 84.22 |
| 500 | 114.0 | 93 | 153 | 1.7 | 3.0 | 0.880 | 88.0 | 68.65 |

**Table 7. Surface composition (weight %) of aluminum before and after immersion in 0.5 M HCl without and with 500 ppm of Ziziphus Spina Christi extract at 25 $^0$C**

| (Mass %) | Al | C | O | Si |
|---|---|---|---|---|
| Pure | 73.24 | 26.4 | - | 0.27 |
| Blank | 90.32 | 9.23 | - | 0.45 |
| inhibitor | 69.17 | 24.29 | 5.94 | 0.60 |

## Discussion

Corrosion inhibition of aluminum in 0.5 M HCl by the extract as indicated from chemical and electrochemical techniques was found to depend on concentration and the nature of extract. It is generally, assumed that adsorption of the inhibitor at the metal /solution interface is the first step in the action mechanism of the inhibitors in aggressive acid media. Four types of adsorption may take place during the inhibition involving organic molecules at the metal/solution interface [58]. Electrostatic attraction between charged molecules and charged metal, interaction of unshared electrons pairs in the molecules, interaction of π electrons with the metal and combination of the above. In discussing corrosion inhibition by surface –active organic compounds, various factors including the number and types of adsorbing groups and their electron structure are taken into consideration. Inhibitor molecules may either be physically or chemically adsorbed on the surface of a corroding metal. Physisorbed molecules are attached to metal at local cathodes and retard corrosion by shifting the cathode reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached [59]. There is a general consensus by several authors that the more negatively charged on heteroatoms is, more is its ability to adsorb on the metal surface through a donor-acceptor type reaction [60]. It is well known that the aluminum surface is positively charged in acid solution [61]. So it is difficult for the protonated molecules to approach the positively charged Al surface due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, thus they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged extract molecules, the protonated extract molecules adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus there is a synergism between adsorbed $Cl^-$ ions and protonated extract molecules. Thus we can conclude that inhibition of Al corrosion in 0.5 M HCl is mainly due to electrostatic interaction. The decrease in inhibition efficiency with rise in temperature supports electrostatic interaction. Extract component molecules contain many compounds possess several heteroatoms (mainly oxygen atoms) containing active constituents, and therefore there may be a synergism between the molecules accounting for the good inhibition efficiencies.

## Conclusions

Ziziphus Spina Christi act as a good inhibitor for the corrosion of aluminum in 0.5 M HCl. Inhibition efficiency increases with the extract concentration, while decrease with the temperature. The negative values of $\Delta G^o_{ads}$ show the spontaneity of the adsorption. Potentiodynamic polarization measurement show that, this extract acts as mixed type inhibitor. EFM appears capable of monitoring the corrosion inhibition of aluminum in 0.5 M HCl solution in the presence of Ziziphus Spina Christi extract. Corrosion current densities ($i_{corr}$) obtained using this technique was in good agreement with those obtained from Tafel extrapolation technique. In addition the causality factors were good internal check for verifying the validity of data obtained by this technique. EIS measurement reveals that charge transfer resistance increases and the double layer capacitance decreases with increase in concentration of the extract. The SEM reveals the formation of a smooth surface on aluminum in presence of Ziziphus Spina Christi probably due to the formation of an adsorptive film of electrostatic character.

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