

## Use of *Capparis decidua* Extract as a Green Inhibitor for Pure Aluminum Corrosion in Acidic Media

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The aim of this paper is to study corrosion inhibition of Aluminum with *Capparis decidua* extract. The study was performed in a 1.0 M solution of hydrochloric acid (HCl) and was monitored both by measuring mass loss and by using electrochemical and polarization methods. A scanning electron microscopy (SEM) technique was also applied for surface morphology analysis. The results revealed high inhibition efficiency of *Capparis decidua* extract. Our data also determined that efficiency is governed by temperature and concentration of extract. Optimum (88.2%) inhibitor efficiency was found with maximum extract concentration at 45°C. The results also showed a slight diminution of aluminum dissolution when the temperature is low. Based on the Langmuir adsorption model, *Capparis decidua* adsorption on the aluminum surface shows a high regression coefficient value. From the results, the activation enthalpy ( $\Delta H^\ddagger$ ) and activation entropy ( $\Delta S^\ddagger$ ) were estimated and discussed. In conclusion, the study clearly shows that *Capparis decidua* extract acted against aluminum corrosion in acidic media by forming a protective film on top of the aluminum surface.

**Keywords:** Aluminum corrosion, Aluminum corrosion inhibition, Corrosion inhibitor, Green corrosion inhibitor, Organic extract corrosion inhibitor

### 1. Introduction

There has been a noticeable high demand for corrosion prevention using organic coatings as potential substitutes for the traditional coatings most of which are inefficient and costly. Recent reports have been showing many advances in the corrosion protecting effect of several types of organic coating systems. Many of these coating systems provided both a barrier and active protection for different metallic structures and corrosion zones. Recently, there have been many examples of organic molecules demonstrating effective adhesion and can be attached to virtually most metals' surfaces to form a stable protective coating. More specifically, examples for aluminum corrosion protection include the use of homologous straight chain mono- and dicarboxylates [1,2], phosphate-based organic molecules [3], aryl pyrroles [4], benzotriazole and phosphono derivatives

[5], and Schiff bases [6]. Other related examples also include the use of natural products and organic extracts, including crude extracts, such as *Kola nitida* extract [7], *Delonix Regis* [8], *Vernonia amygdalina* [9], and Rosemary leaves [10].

Metal corrosion inhibition using organic compounds happens through the formation of a protecting film by means of chemisorption, or adsorption, of organic substances on the metal exterior. Corrosion of metals can considerably decrease as a result. Adsorption level is determined by the nature of the metal and the corrosive media [11]. Many reports have been published illustrating the efficiency of natural organic compounds extracted from plants that act as good metal corrosion inhibitors [12-16]. Most of these repeatedly mentioned heterocyclic molecules that contain nitrogen, oxygen, phosphorus, and sulfur which show higher tendency of adsorption [17-19]. Aluminum corrosion, including aluminum alloys corrosion, has been getting a lot of attention in more

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recent metal corrosion studies due to its industrial importance. For that reason, more recent research has been focused on utilizing such organic substances to inhibit corrosion of aluminum and alloys [20-33]. Natural products from plants have been showing very promising results as inexpensive and green corrosion inhibitors. A wide range of organic compounds has been extracted from plants including the leaves, roots, seeds, and barks which can be used as effective metal corrosion inhibitors [24-26]. *Capparis decidua* extract efficiency in inhibiting corrosion can be ascribed to the occurrence of a mixture of organic compounds. However, all studied extracts prominently contained phenolics and glucocinates.

In this study, *Capparis decidua* extract corrosion inhibition of aluminum is studied using methods of weight loss and electrochemical polarization in 1.0 M Hydrochloric acid solution. The effect of the concentration of inhibitor and temperature on the efficiency was studied and determined. Scanning electron microscopy (SEM) technique was applied to analyze the surface morphology.

## 2. Experimental

### 2.1. Collection and Pretreatment of Plant Extract

*Capparis Decidua* plant was collected from the Dead Sea area during the flowering season (April-May). All collected samples were identified by Prof. Jamil Laham (Department of Biological Sciences, Faculty of Sciences, Yarmouk University). All samples were washed under running water and then dried for 25 days. The dried plant was ground into powder before extraction.

### 2.2. Material preparation

Aluminum samples with high purity (99.999%) were obtained as a foil with thickness at 0.5 mm (Sigma-Aldrich). All the experiments were performed using aluminum foil samples (dimensions: 3.0 cm × 1.0 cm × 0.5 mm). Aluminum samples were mixed with a solution containing 85% H<sub>3</sub>PO<sub>4</sub> (weight%) in water and 15% HNO<sub>3</sub> (volume%) at 80 - 85 °C for about 30-35 sec followed by immersing in 50% HNO<sub>3</sub> solution (volume%) at 50-55 °C for 20-25 sec. Samples were then rinsed thoroughly with deionized water.

### 2.3. Sample preparation for weight-loss measurements

Aluminum corrosion inhibition efficiency in HCl aqueous solution by *Capparis decidua* extract was determined using gravimetric analysis. An amount of 50 g of dry *Capparis decidua* powder was heated to reflux in 0.25 L HCl solution (1.0 M) for 3.0 h. Solution was then let to stand overnight after which was filtered. Mass-loss tests were performed with aluminum foil samples with total surface area of 6.4 cm<sup>2</sup>. Samples were weighed and immersed for (1, 2, 4 and 6 hours) at 25 °C in 15 mL of 1.0 M HCl solutions of *Capparis decidua*, and at varying concentrations of the extract (40-440 mg/L). After being tested, samples were then washed with water and then weighed after drying. These measurements were done at temperatures 25, 35, and 45 °C using a water bath. Experiments were repeated three times each to report only reproducible data.

### 2.4. Potentiostatic polarization measurements

For this purpose, we used the “EG&G-model 264” potentiostat-galvanostat, potentiostatic polarization method. Potentiodynamic polarization tests were constructed based on data obtained from three-electrode conventional cell. Working electrode was a cylindrical-shaped aluminum bar inserted in araldite with exposed area of 0.6 cm<sup>2</sup>. Reference electrode was simply a saturated calomel electrode, or SCE, and for counter electrode platinum foil was used. Polarization was studied in an acidic medium both with and without *Capparis decidua* at different concentrations of the latter. Potentiodynamic polarization tests were constructed and polarization was monitored for potential range between -1000 mV and 0 mV through a scan rate of 10 mV s<sup>-1</sup>.

Applying the Stern-Geary equation, the current density of electrochemical corrosion was estimated as the following:

$$I_{corr} = \beta_a \beta_c / (2.3 R_p (\beta_a \beta_c)) \quad (1)$$

Where  $I_{corr}$  represents the density of corrosion current,  $\beta_a$  and  $\beta_c$  represent anodic and cathodic Tafel constants, and  $R_p$  represents the polarization resistance.

$I_{corr}$  was determined from intercepting anodic-cathodic Tafel lines. Efficiency of inhibition, or  $I\%$ , was determined from the equation below:

$$I\% = I_{corr}^* - I_{corr} / I_{corr}^* \quad (2)$$

Where,  $I_{corr}^*$  and  $I_{corr}$  represent the current densities of corrosion without inhibitor and with inhibitor, respectively.

### 2.5. Scanning electron microscopy (SEM)

The surface morphology of samples was tested in a procedure that involved exposure to 1.0 M HCl. Conditions applied were both in the absence and presence of the inhibitor where optimized concentration in the latter was applied. Instrument used was FEI-Inspect F50 scanning electron microscope that had a field-emission gun.

## 3. Results and Discussion

### 3.1. Mass-loss measurement

#### 3.1.1. Effect of inhibitor concentration

Aluminum weight loss in 1.0 M HCl was determined both with and without using *Capparis decidua* at 25 °C, at different immersion times (1, 2, 4, and 6 hr), and different extract concentrations (40-440 mg/L). Mass loss was reported to the closest  $\pm 1 \times 10^{-4}$  g. Aluminum mass reduction caused by the corrosive solution was determined using the following equation:

$$\Delta W = W_i - W_f \quad (3)$$

Where  $W_i$  and  $W_f$  represent the mass reduction of aluminum samples with and without inhibitor, respectively. Fig. 1 illustrates changes in mass-loss (mg) of aluminum from corrosion at different dipping periods and 1.0 M HCl at different concentrations of inhibitor at 25 °C. Aluminum mass-loss was measured at different time rests without and with varying concentrations of *Capparis decidua* extract. Weight-loss values of aluminum (mg) went down when the inhibitor concentration was higher. This indicates that corrosion inhibition gets better upon increasing extract concentration. Such an observation was expected since there is more of the metal surface is being covered upon increasing extract concentration [27,32].

The percentage efficiency of inhibition (%IE) and the

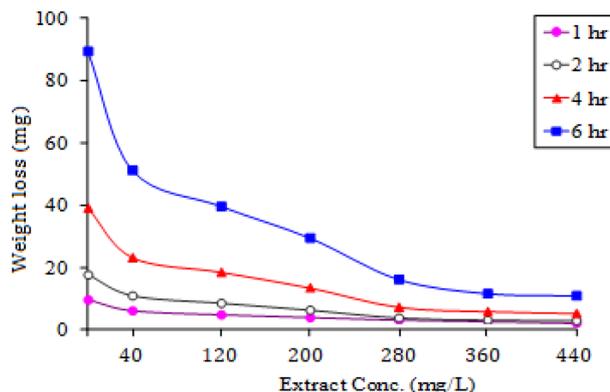


Fig. 1. Weight-loss changes of aluminum Vs. *capparis decidua* extract concentration (measurements done in 1.0 M HCl at 25 °C and different dipping time intervals)

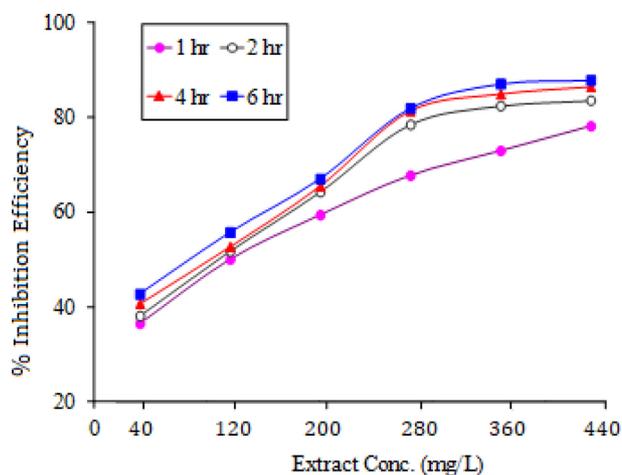


Fig. 2. Change of inhibition efficiency of aluminum corrosion (%IE) against time in 1.0 M HCl at different concentration of inhibitor and 25 °C

amount of surface coverage ( $\theta$ ) of the studied *Capparis decidua* crude extract are shown in Fig. 2. The Fig. illustrates the change in inhibition efficiency with and without inhibitor in acidic medium. Experiments were done at different time intervals using varied inhibitor concentrations at 25 °C. A closer look at these figures indicates that efficiency of inhibition is higher when increasing both extract concentration and dipping time. Surface coverage, that is directly proportional to efficiency of inhibition ( $f = 0.1 * \%IE$ ), was observed to be higher when the concentration and time were both higher. In general, adsorption of inhibitor molecules at metal-solution interface can significantly alter corrosion resistance by the metal. The ability of organic substances to be corrosion inhibitors is mainly governed by their adsorption

**Table 1. Inhibition efficiencies of aluminum corrosion at different concentrations of inhibitor, at different time intervals, and 25 °C**

| Medium    | Conc. (ppm) | Inhibition Efficiency (%IE) |        |        |        |
|-----------|-------------|-----------------------------|--------|--------|--------|
|           |             | (1 hr)                      | (2 hr) | (4 hr) | (6 hr) |
| 1.0 M HCl | 40          | 36.5                        | 38.1   | 40.7   | 42.7   |
|           | 120         | 50.0                        | 51.7   | 52.7   | 55.7   |
|           | 200         | 59.4                        | 64.2   | 65.5   | 67.0   |
|           | 280         | 67.7                        | 78.4   | 81.3   | 81.9   |
|           | 360         | 72.9                        | 82.4   | 84.9   | 87.0   |
|           | 440         | 78.1                        | 83.5   | 86.4   | 87.8   |

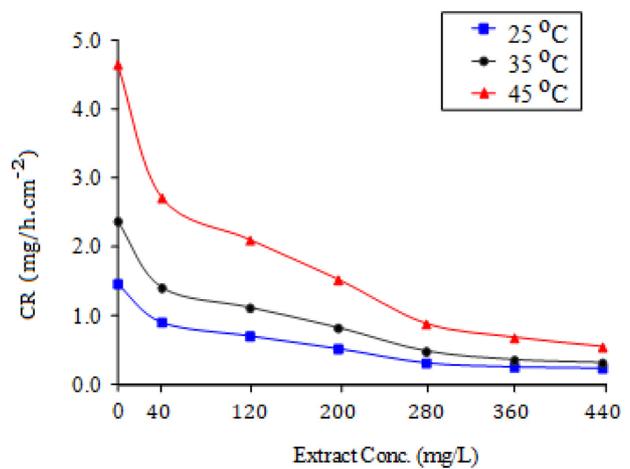
aptitude. Adsorption of organic inhibitor molecules occurs through swapping water molecules [27].

### 3.1.2. Effect of temperature

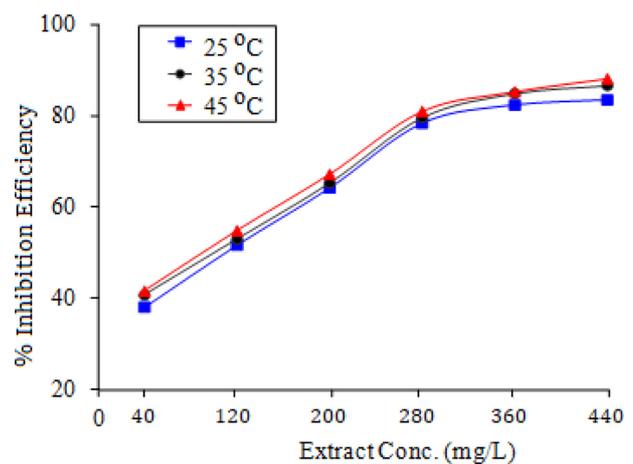
The best approach to comprehend the mechanism by which inhibition of corrosion happens is by detecting the effect of temperature. Temperature affects the rate of corrosion and hence inhibition efficiency was examined so as to know the nature of absorption of the inhibitor. Altered experiments were performed using similar experimental conditions where the temperature was different. Experiments were performed at 25, 35, and 45 °C. Immersion time in all experiments was upheld at 2.0 hours. The results obtained from changing temperature the effect of that on corrosion rate of aluminum in 1.0 M of HCl are shown in Fig. 3.

Fig. 3 demonstrates that corrosion rates are directly proportional to temperature. Normally, rate of metal corrosion and/or rate of metal dissolution increases with increasing temperature. When inhibition efficiencies were calculated, however, the opposite results were observed. That is, efficiency of inhibitor was observed to be better upon increasing temperature as shown in Fig. 4. According to many reports in the literature, if increasing the temperature leads to lower inhibitor efficiency, this is normally indicative of the physical, electrostatic, formation of an adsorption film. Our study, however, is showing the opposite behavior; that is slightly the increase of the inhibitor efficiency with increasing temperature. This later observation strongly suggests a chemisorption mechanism instead [28-30].

Table 2 presents the inhibition efficiencies of the extract at various inhibitor concentrations. Experiments



**Fig. 3. The variation in corrosion speed of Al in 1.0 M HCl using *Capparis decidua* crude at various temperatures**



**Fig. 4. The change in inhibitor efficiency with inhibitor concentration for aluminum corrosion in 1.0 M HCl using *Capparis decidua* extract at different temperatures**

were done in 1.0 M HCl, for 2.0 hours dipping time and a temperature range of 25-45 °C. Results clearly show

**Table 2. Inhibition efficiencies of Al in the presence of different concentrations of the inhibitor at different temperatures at 2 hr**

| Medium    | Conc. (ppm) | Inhibition Efficiency (%IE) |            |            |
|-----------|-------------|-----------------------------|------------|------------|
|           |             | T= 25 °C K                  | T= 35 °C K | T= 45 °C K |
| 1.0 M HCl | 40          | 38.1                        | 40.7       | 41.6       |
|           | 120         | 51.7                        | 53.0       | 54.8       |
|           | 200         | 64.2                        | 65.3       | 67.2       |
|           | 280         | 78.4                        | 79.6       | 81.0       |
|           | 360         | 82.4                        | 84.9       | 85.3       |
|           | 440         | 83.5                        | 86.7       | 88.2       |

that inhibitor efficiency gets higher when the inhibitor concentration goes up from 40 to 440 mg/L. Maximum inhibition efficiency of 88.2% was obtained at 45 °C and using 440 mg/L of the extract. This most probably is a result of larger area of the metal surface being covered by the extract and prevented from corrosion.

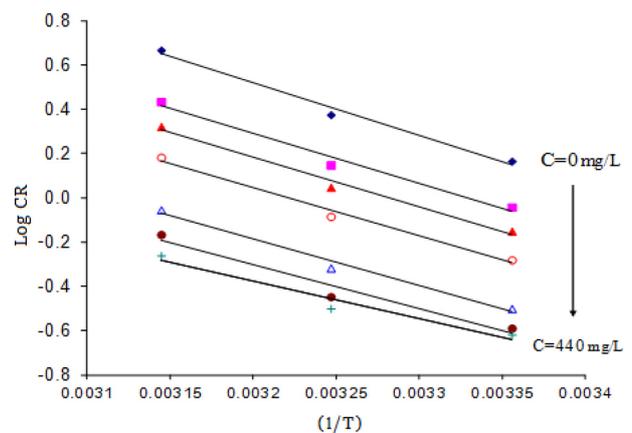
3.1.3. Kinetic and thermodynamic considerations

Temperature effect on inhibitor efficiency was thoughtfully studied in order to define the kinetics and mechanism of action. As the data above show, increasing temperature from 25 °C to 45 °C, while using the inhibitor, resulted in an increase in rate of corrosion. Plugging these results into Arrhenius equation below using that temperature range, a plot was established for the logarithm of corrosion rate, log [CR], versus the reciprocal of absolute temperature, 1/T, resulted in a straight line:

$$R_c = Ae^{\frac{-E_a}{RT}} \tag{4}$$

Where  $R_c$  represents corrosion rate,  $E_a$  represents the energy of activation, and  $A$  represents the frequency factor (constant). Plots are shown in Fig. 5 for 1.0 M HCl solution with and without the inhibitor.

Calculated  $E_a$  values are summarized in Table 3. As shown in the table, values of  $E_a$  are inversely proportionate to inhibitor concentration. In addition,  $E_a$  shows higher



**Fig. 5. Arrhenius plots of aluminum corrosion in 1.0 M HCl without and with different concentrations of inhibitor extract at 2 hours**

**Table 3. Corrosion rates (mg/h.cm<sup>2</sup>) and activation energies at a number of temperatures in 1.0 M HCl**

| Conc. (mg/L) | CR      | CR      | CR      | R <sup>2</sup> | Ea (kJ/mol) |
|--------------|---------|---------|---------|----------------|-------------|
|              | (25 °C) | (35 °C) | (45 °C) |                |             |
| 0            | 0.266   | 0.432   | 0.845   | 0.985          | 45.54       |
| 40           | 0.165   | 0.256   | 0.494   | 0.979          | 43.21       |
| 120          | 0.129   | 0.203   | 0.366   | 0.989          | 41.31       |
| 200          | 0.095   | 0.151   | 0.254   | 0.995          | 38.59       |
| 280          | 0.058   | 0.089   | 0.145   | 0.994          | 36.62       |
| 360          | 0.047   | 0.065   | 0.109   | 0.976          | 33.22       |
| 440          | 0.044   | 0.057   | 0.101   | 0.951          | 32.36       |

values in uninhibited conditions compared to the inhibited ones. A closer look at how temperature affects inhibitor efficiency combined with  $E_a$  values of the corrosion process provides some leads to the nature of inhibitor adsorption mechanism [18-20].

Determining how spontaneous a metal converts into its corrosion products is governed by thermodynamic parameters. Namely, these parameters of activation include enthalpy ( $\Delta H^\ddagger$ ), entropy ( $\Delta S^\ddagger$ ), and free energy ( $\Delta G$ ) were calculated using the modified Arrhenius equation of transition state:

$$R_c = \frac{K_b \cdot T}{\square} \cdot e^{(\Delta S^\ddagger/R)} \cdot e^{(-\Delta H^\ddagger/RT)} \quad (5)$$

Where  $K_b$  represents Boltzmann constant,  $\Delta H^\ddagger$  is the enthalpy of activation,  $h$  is Planck's constant, and  $\Delta S^\ddagger$  is the entropy of activation. Fig. 6 illustrates the linear result of plotting  $\text{Log} [R_c/T]$  Vs.  $(1/T)$ . Table 4 presents  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  calculated values based on the graph.

Enthalpy of activation,  $\Delta H^\ddagger$ , absolute values went down from 45.54 kJ/mol to 32.36 kJ/mol while conditions changed from uninhibited medium for maximum inhibitor concentration of 440 mg/L in 1.0 M HCl. This observed decrease in  $\Delta H^\ddagger$  of upon increasing the inhibitor concentration, with the fact that  $\Delta H^\ddagger$  of inhibited medium is lower the uninhibited counterpart, indicates chemical adsorption inhibitory action. Nevertheless, our obtained  $\Delta H^\ddagger$  values are greater than those known related to common physical adsorption and lower than values related to common chemical adsorption [21,22]. This observation is suggestive of a comprehensive adsorption that includes both chemical and physical adsorption. The justification to this is the fact that enthalpy is very similar to the chemical process analogue. It is known that absolute values of enthalpy of activation ( $\Delta H^\ddagger$ ) below 42.0 kJ mol<sup>-1</sup> indicate a physical adsorption whereas when these get near 100 kJ mol<sup>-1</sup> that indicates a chemical adsorption [19]. Based on the abovementioned, our hypothesis that *Capparis decidua* inhibits corrosion in 1.0 M HCl via physical adsorption predominates.

Entropy of activation,  $S^\ddagger$ , was less than zero for both cases; with and without inhibitor. The decrease in entropy at transition state is indicative of association

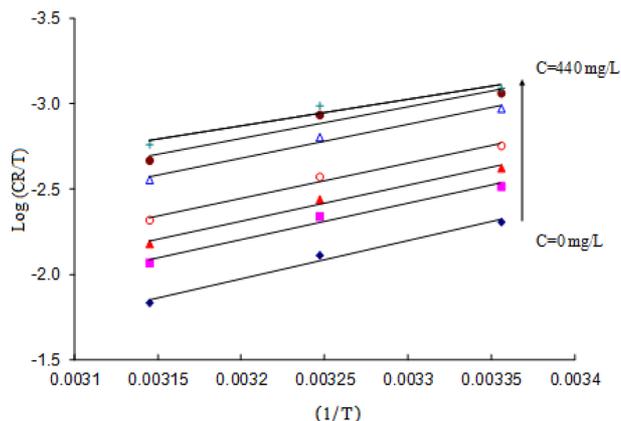


Fig. 6. Plot of  $\log CR/T$  vs  $1/T$  for *Capparis decidua* extract in 1.0 M HCl

Table 4. Enthalpy and Entropy values of the reaction with various concentrations of the *Capparis decidua* extract in 1.0 M HCl

| Inh. Conc. (mg/L) | R <sup>2</sup> | $\Delta S^\ddagger$ (kJ/mol. K) | $\Delta H^\ddagger$ (kJ/mol) |
|-------------------|----------------|---------------------------------|------------------------------|
| 0                 | 0.984          | -0.087                          | 42.974                       |
| 40                | 0.977          | -0.098                          | 40.647                       |
| 120               | 0.988          | -0.107                          | 38.752                       |
| 200               | 0.994          | -0.118                          | 36.035                       |
| 280               | 0.993          | -0.129                          | 34.057                       |
| 360               | 0.972          | -0.142                          | 30.662                       |
| 440               | 0.943          | -0.146                          | 29.798                       |

rather than dissociation in the rate determining step due to a diminution in randomness upon reaching the activated complex moving from reactants [33,34]. This observed ordered behavior  $\Delta S^\ddagger$  produces negative values of  $\Delta S^\ddagger$  when the inhibition efficiency is increased. This also can be seen more prominently when the study included HCl inhibited solutions. The explanation to producing a more ordered system could be that inhibitor species are involved in the activated complex of the corrosion reaction.

### 3.2. Adsorption behavior

We can determine the adsorption isotherm if the inhibitor which acts mainly via adsorption on the surface of metal. The inhibitory action of *Capparis decidua* extract on aluminum corrosion in acidic medium can be ascribed to adsorption on aluminum surface. The observed decrease in corrosion rate was obtained by the inhibitor acting as a blockade between the solution

surface and metal.

Values of inhibitor amount adsorbed from solution onto aluminum,  $Q_{ads}$ , is calculated using the equation below [35,36]:

$$Q_{ads} = 2.303R \left[ \log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right) \right] \left[ \frac{T_1 T_2}{T_2 - T_1} \right] \quad (6)$$

$R$  represents the gas constant,  $\theta_1$  and  $\theta_2$  are the extent of surface being covered at respective temperatures  $T_1$  (324K) and  $T_2$  (335K).

$Q_{ads}$  calculated values were found to be in the range between 0.147 and 0.612 kJ/mol for acidic medium. Positive values of  $Q_{ads}$  specifies an efficiency increase at higher temperatures [37].

Experimental results for the examined *Capparis decidua* extract as an inhibitor in acidic solution were plugged-in a number of adsorption isotherms among which best correlation fitted in the equation below which represents Langmuir adsorption isotherm:

$$\log(C/\theta) = -\log K_{ads} + \log C \quad (7)$$

$C$  represents concentration of inhibitor in units of ppm and  $K$  is the adsorption equilibrium constant of inhibitor on the metal surface. The plot of  $\text{Log}[C/\theta]$  vs  $\text{Log}[C]$  fitted the experimental data for the acidic solution as shown Fig. 7.

Equilibrium constant values,  $K_{ads}$ , of adsorption at varied temperatures were determined from the above linear plot (Fig. 7) and are summarized in the table below (Table 5).

As it can be seen, values are less than zero and averaged at -4.66 kJ/mol. The result suggests the inhibitor adsorption on aluminum exterior is a

spontaneous process and also does confirm the anticipated mechanism of physical adsorption.

Moreover, it was detected that the value of  $K_{ads}$  goes higher upon increasing temperature. This indicates that adsorption of inhibitor was more favored at higher temperatures. This observation suggests that adsorbed inhibitor molecules interact more strongly with metal exterior at higher temperature up to 45 °C. This explains why at higher temperatures increase in inhibitor efficiency was observed. However, this study has showed low values of free energy change  $\Delta G_{ads}$ . This confirms a physisorption mechanism of the *Capparis decidua* as an inhibitor on aluminum surface.

Experimental results from the tested inhibitor have been plugged into Temkin adsorption isotherm:

$$e^{a\theta} = KC \quad (8)$$

Fig. 8 shows a plot of  $\theta$  versus  $\log[C]$  that was constructed from data obtained by Temkin equation. The obtained linear plot confirms Temkin adsorption isotherm behaviour of *Capparis decidua* extract on aluminum surface. The fitting gave excellent results

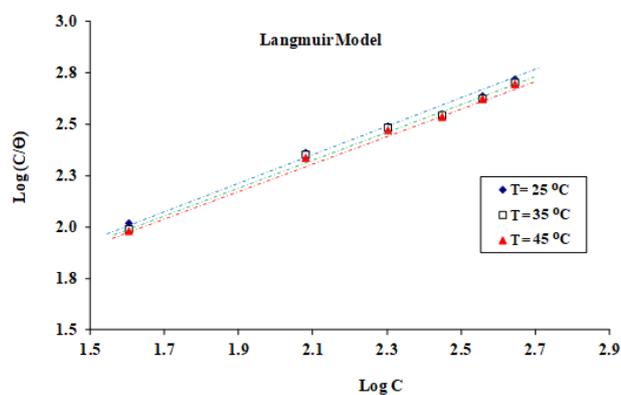


Fig. 7. Langmuir adsorption of *Capparis decidua* extract on aluminum surface (done at 1.0 M HCl for 120 minutes and altered temperatures)

Table 5. Langmuir adsorption parameters for the adsorption of *Capparis decidua* extract on aluminum in acidic medium for 120 min immersion period at different temperatures

| Langmuir Isotherm | Temperature (°C) | $K_{ads}$ | $R^2$  | $\Delta G_{ads}$ (kJ/mol) |
|-------------------|------------------|-----------|--------|---------------------------|
| Acidic            | 25               | 0.110     | 0.9942 | -4.29                     |
|                   | 35               | 0.113     | 0.9934 | -4.71                     |
|                   | 45               | 0.119     | 0.9954 | -4.99                     |

where  $R^2$  was greater than 0.96. Values of  $K_{ads}$  and  $\Delta G_{ads}$  were estimated and are presented in Table 6.

The association between adsorption equilibrium constant,  $K$ , and adsorption free energy,  $\Delta G_{ads}$ , is described in the following equation:

$$\Delta G_{ads} = -2.303RT \text{Log}(55.5K) \quad (9)$$

Adsorption free energy figures,  $\Delta G_{ads}$ , of crude on aluminum surface have been determined using isotherms plot in Fig. 8 and are reported in Table 6. These values were -7.62, -7.92, and -8.32 kJ/mol at 45, 35, and 25 °C, respectively. Values mean the adsorption of crude *Capparis decidua* occurs via mechanism of physical adsorption that also happens to be spontaneous. Commonly, values of  $\Delta G_{ads}$  up to -20 kJ/mol, like the

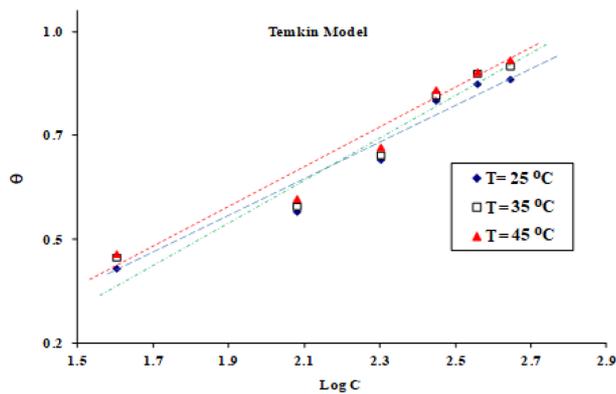


Fig. 8. Temkin adsorption isotherm:  $\log C$  vs.  $\theta$ . for *Capparis decidua* crude at varied temperatures for the corrosion of aluminum in 1.0 M HCl

Table 6. Temkin adsorption parameters

| Temkin Isotherm | Temperature (K) | $K_{ads}$ | $R^2$ | $\Delta G_{ads}$ (kJ/mol) |
|-----------------|-----------------|-----------|-------|---------------------------|
| acidic          | 25              | 0.992     | 0.990 | -9.93                     |
|                 | 35              | 1.148     | 0.994 | -10.64                    |
|                 | 45              | 1.303     | 0.994 | -11.32                    |

Table 7. Electrochemical corrosion parameters of Aluminum without and with varied concentration of *Capparis decidua* in 1.0 M HCl

| [inhibitor] (mg/L) | $E_{corr}$ (V/sec) | $I_{corr}$ (mA/cm <sup>2</sup> ) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | I%       |
|--------------------|--------------------|----------------------------------|--------------------|--------------------|----------|
| Blank              | -0.8107            | 0.7848                           | 0.045              | 0.168              | -        |
| 120                | -0.7797            | 0.2867                           | 0.027              | 0.062              | 63.4684  |
| 280                | -0.7584            | 0.1846                           | 0.025              | 0.091              | 76.4781  |
| 440                | -0.7527            | 0.1089                           | 0.036              | 0.062              | 86.12385 |

ones found in our study, correspond to physical adsorption. However, values of  $\Delta G_{ads}$  that are smaller than -40 kJ/mol point toward chemical adsorption [26].

### 3.3. Potentiostatic polarization measurements

Polarized cathodic/anodic potentials, have been determined with and without using *Capparis decidua* at different concentrations. Corrosion current density range was 0.70-7.00 A/cm in HCl. Fig. 9 is showing polarization curves, cathodic/anodic, of aluminum with and without using inhibitor. When the inhibitor was in use, diverse concentrations were applied in 1.0 M HCl.

#### 3.3.1 Electrochemical corrosion

Electrochemical parameters of corrosion, such as corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ), inhibitor efficiency (I%), and cathodic/anodic Tafel constants ( $\beta_c$  and  $\beta_a$ ), and, were all determined

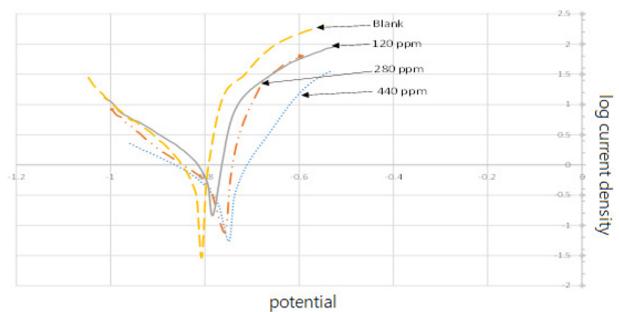


Fig. 9. Anodic and cathodic polarization curves of aluminum in 1.0 M HCl without and with varied concentrations of *Capparis decidua*

from polarization curves and are summarized in Table 7. Parameters shown by the table above show that current density of corrosion has been significantly reduced upon increasing inhibitor concentration. This points to that *Capparis decidua* has a noticeable corrosion inhibition effect on aluminum in these media. In addition, from the polarization curve presented in Fig. 9, one can notice that inhibition occurred for both cathodic and anodic reactions.

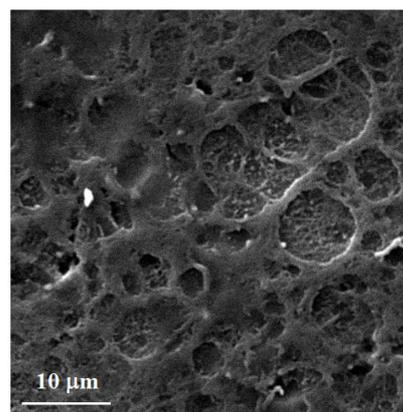
It is also perceptible from results described in Table 7 that when increasing the inhibitor concentration, corrosion potential ( $E_{\text{corr}}$ ) has somewhat changed and in turns smaller values of corrosion current density ( $I_{\text{corr}}$ ) were found. Additionally, the values for anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ ) Tafel constants were more significantly affected by using *Capparis decidua*. This result is in favor of a mixed type inhibitor.

Data presented in Table 7 demonstrates that  $\beta_a$  is larger than  $\beta_c$  at any inhibitor concentration which can tell that anodic polarization is affected to a larger extent by the inhibitor.

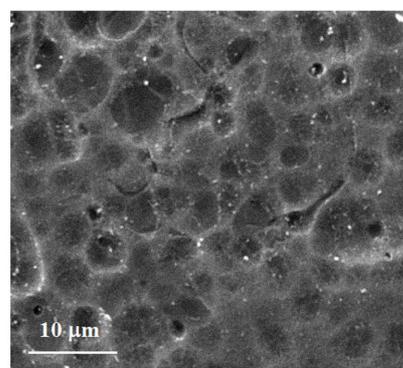
Moreover, assessment of Table 7 can tell that current densities ( $I_{\text{corr}}$ ) decrease substantially by addition of extract to the acidic solution in comparison to blank solution. This observation specifies that the inhibitor slows down the speed of corrosion. In addition, a substantial reduction in corrosion current ( $I_{\text{corr}}$ ) and corrosion speed was together with a rise in polarization resistance ( $R_p$ ) value, which tells that inhibitor effectiveness improved with extract concentration and up 440 ppm. Values of inhibitor efficiency ( $I\%$ ) acquired from the polarization experiment are consistent with results found in the mass-loss experiment with little difference. The outcomes from those experiments can demonstrate that *Capparis decidua* provided reasonable protection for aluminum counter to corrosion in acidic solutions. This behavior can be credited to the stability of inhibitor layer that was formed on aluminum exterior [37,39].

### 3.4 Scanning electron microscope (SEM)

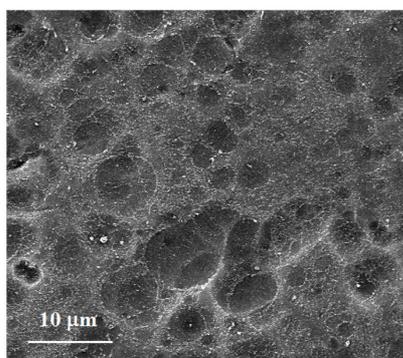
Fig. 10a shows an even and major corrosion without inhibitor which also resulted in the formation of the corrosion product. Formation of those corroded areas can be ascribed to dissolution of aluminum caused by



(a)



(b)



(c)

**Fig. 10.** Scanning electron micrograph (100 $\mu\text{m}$ ) of pure aluminum in acidic medium (a) in 1.0 M HCl at 25 °C (b) in 1.0 M HCl and 120 ppm *Capparis decidua* at 25 °C (c) in 1.0 M HCl and 440 ppm *Capparis decidua* at 25 °C

$\text{H}^+$  ions attack and the extra acidity of solution near aluminum exterior [40]. In contrast, results show that aluminum corrosion reduced significantly by using the inhibitor where aluminum exterior has been partly coated with inhibitor. We also observed that this film has formed in the presence of Hydrochloric acid (Fig. 10b and c). To support the concept of formation of a

protective film of inhibitor, scanning electron micrographs were carefully analyzed (Fig. 10c).

#### 4. Conclusions

The following are the key conclusions that can be pinched from this study:

1) Data obtained by mass-loss and polarization experiments confirm the likely usefulness of *Capparis decidua* crude as a green inhibitor of aluminum corrosion in acidic medium

2) Inhibitor effectiveness was higher when concentration of *Capparis decidua* crude was increased at a maximum value of 440 ppm at 45 °C, and inhibitor effectiveness was also higher at higher temperature.

3) The energy of activation,  $E_a$ , of aluminum dissolution in acidic solution without the inhibitor was found to be higher than that with inhibitor. This means that aluminum corrosion inhibition by *Capparis decidua* occurred via both barrier protection and passivation mechanisms.

4) Equilibrium isotherms of adsorption of *Capparis decidua* on aluminum in HCl at different temperatures were analyzed using two widely used isotherm models; Langmuir and Temkin isotherm models.

5) Value of Gibbs free energy change showed that inhibition mechanism is attributed to physical adsorption in acidic media and its sign indicates that the process is spontaneous.

6) Polarization results displayed that *Capparis decidua* is a mixed-type anodic/cathodic inhibitor.

7) SEM data indicated that aluminum exterior is partly coated with inhibitor molecules resulting in a practical level of protection.

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