# Khillah Extract as Green Corrosion Inhibitor for Zinc in Aqueous Solutions

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**ABSTRACT**

In this work, Khillah extract was examined as green corrosion inhibitor for zinc in 3.5 % NaCl and 16 ppm solution by using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Results obtained showed that the extract of Khillah functioned as an effective and good inhibitor. The inhibition efficiency was found to increase with increase of extract concentration reaching maximum inhibition efficiency 87.2%. The adsorption of the inhibitor molecules on the zinc metal surface obeyed Langmuir adsorption isotherm. Polarization data indicated that this extract acts as mixed type inhibitor.

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## Introduction

Zinc is an important metal with numerous industrial applications [1-3] and is mainly used for the corrosion sacrificial protection of steel [4-7]. The zinc coated steel materials provide a greater resistance to corrosion, but when exposed to humid atmosphere, it undergoes rapid corrosion with the formation of corrosion products known as white rust. The formation of the white rust on zinc surface is prevented by the application of chromate treatment [8]. The effluent obtained during chromate treatment induces the environmental pollution. But recent environmental regulations restrict the use of chromate solution and recommended its replacement with other non-toxic, biodegradable and environment friendly natural products of plant origin as corrosion inhibitors [9-19]. Therefore, there is a need for change in the formulation of corrosion inhibition by an increasing demand for reduced environmental impact. Extracts of plant materials containing nitrogen, oxygen and /or sulphur atoms have been used to control the corrosion of Zn and others metals in different corrosion medium such as NaCl , HCl ,….. [20-25].

Khillah is a medicinal plant has been extensively used traditionally to treat various ailments such as urologic, dermatologic, respiratory symptoms, diuretic, carminative, stimulant, antispasmodic, congestion of prostrate gland, urinary diseases, renal stones, circulatory herb used to relax the coronary arteries, and helps to improve blood supply to the heart muscle and thereby eases angina, and also for dental care. The dry umbel rays used as toothpicks [26, 27]. Khillah contains small amount of volatile fatty oil, proteins 13.83 %, cellulose 22.4 % coumarins 0.5 % and furanochromones up to 4 % such as khellin 1.2 % and visnagin 0.3 % [28]. Structures of some of the previously isolated phytoconstituents from Khillah are shown in scheme 1.

In the present work the extract of seeds of Khillah were used as green corrosion inhibitor for zinc metal in 3.5 % NaCl and 16 ppm solution using chemical and electrochemical techniques.
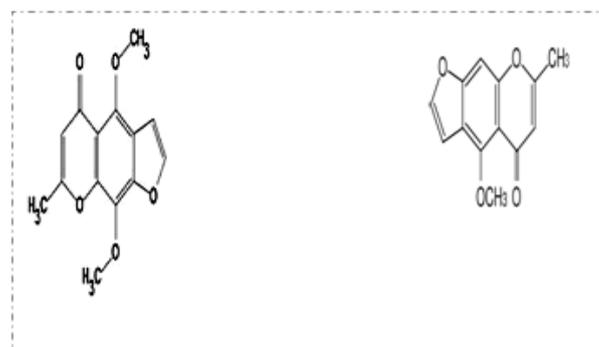


4, 9-Dimethoxy-7-methylfuro[3, 2-g] chromen-5-one **[Khellin]**

4-Methoxy-7-methyl-5H-furo[3, 2 g] [1] benzopyran-5-one **[visnagin]**

**Scheme 1. Chemical structure of selected phytochemicals from *Khillah***

## Experimental

### Material Composition of the Sample

The zinc (BDH grade) used in this investigation has the following chemical composition in weight %:

### Solutions

The corrosion medium employed was 3.5 % NaCl and 16 ppm Na₂S prepared from analytical grade and bidistilled water was used for preparation of the solutions. A stock solution of sodium chloride (3 M) was prepared using bidistilled water. Dissolve 175.5 g of anhydrous sodium chloride in 500 ml freshly prepared distilled water then dilute to 1000 ml with the distilled water then withdrwal 20 ml from stok solution then dilute to 100 ml to prepare 3.5 % sodium chloride. A stock solution of sodium sulfide (1000 ppm) was prepared using bidistilled water. Wash the sodium sulfide crystals with deionized water to remove the

contaminants from oxidation products and blot dry the crystals with a tissue. Dissolve 1 g of anhydrous sodium sulfide in 250 ml freshly prepared distilled water then dilute to 1000 ml with the bidistilled water then withdrwal 1.6 ml from stok solution then dilute to 100 ml to prepare 16 ppm sodium sulfide.

**Preparation of Plant Extract**

The seeds of *khillah* plant were obtained from the local market. It is cleaned with tap water to remove mud particles. Seeds dried in an oven for 2 hours at 100 °C and ground to get the powder form of the material. About 50 g of the powder was soaked in a 250 ml of methanol under cold percolation method and extract by steam distillation for 2 h. The extracted solution was then filtered, concentrated by evaporation on steam bath until it becomes as a sticky sludge. The sludge was left overnight in open air for complete dryness. A stock solution was prepared from the collected solid by weight and used to prepare the desired concentrations by dilution.

**Measuring Methods**

**Weight-loss measurements**

The test pieces were 20 x 20 x 2 mm. The % inhibition efficiency (IE) and the degree of surface coverage (θ) were calculated using equation (1).

% IE = Ө x 100 = [(W$_o$ - W$_i$) / W$_o$] x 100     (1)

Where W$_o$ and W$_i$ are the weight losses per unit area in absence and presence of the extract.

**Electrochemical measurements**

The electrochemical experiments were carried out in a three electrode electrochemical cylindrical Pyrex glass cell with a platinum counter electrode and saturated calomel electrode (SCE) as reference. The working electrode had the form of a square cut from Zn sheet (1 cm$^2$). A duration time 30 min was given for the system to attain a steady state and the open circuit potential (OCP) was noted. Both cathodic and anodic polarization curves were recorded potentiodynamically by changing the electrode potential between- 0.5 V and -2V, at the scan rate of 1 mVs$^{-1}$, the % inhibition efficiency (IE) and degree of surface coverage (θ) were calculated from the electrochemical measurements by equation (2):

% IE = Ө x 100 = [1-(i$_{inh}$/i$_{free}$)] x 100     (2)

Where, i$_{inh}$ is the corrosion current density in presence of extract and i$_{free}$ is the corrosion current density in absence of extract. Experiments for EIS measurements were conducted in the frequency range of 100 kHz to 10mHz at open circuit potential (OCP). The amplitude was 5 mV.

Experiments for EFM measurements were carried out using two frequencies 2 and 5 Hz. The base frequency was 1Hz with 32 cycles, so the waveform repeats after 1s. A perturbation signal with amplitude of 10 mV was used. The electrochemical measurements were carried out using Potentiostat /Galvanostat / Zera analyzer (Gamry PCI 300/4). This includes Gamry framework system based on the ESA400, and a personal computer with DC 105 software for potentiodynamic polarization, EIS 300 software for EIS, and EFM 140 software for EFM measurements. Echem Analyst 5.58 software was used for plotting, graphing, and fitting data.

**Results and discussion**

**Weight loss measurements**

**Effect of extract concentrations and immersion time**

The weight losses of zinc in 3.5 % NaCl and 16 ppm Na$_2$S in absence and presence of different concentrations of *Khillah* extract (50 - 500 ppm), were determined at different times of immersion (30 to 180 min.) at 30 °C. Table (1) reveals that the values of the inhibition efficiency increased with increasing of

*Khillah* extract concentration this behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of extract with the increase of its concentration. To elucidate the influence of immersion time on the corrosion rate of zinc, the data as shown in Figure (1) the weight loss of zinc enhances with immersion time. On the other hand, by increasing the concentration of *Khillah* extract, the weight losses of zinc samples are decreased. This means that *Khillah* extract act as inhibitor.
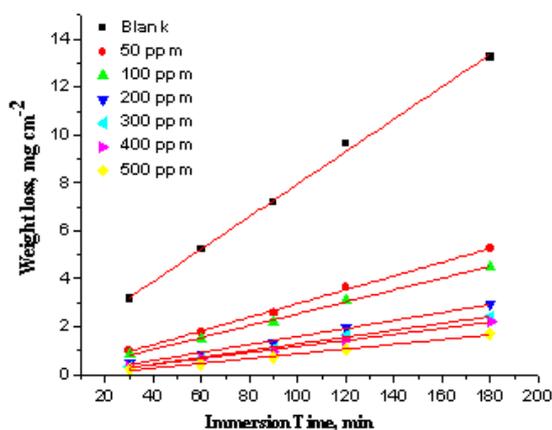


**Figure 1. Weight-loss versus immersion time for Zn in 3.5% NaCl and 16 ppm Na$_2$S solution in the absence and presence different concentrations of Khillah at 30°C**

**Adsorption Isotherm**

To study the mechanism of *Khillah* corrosion inhibition, attempts were made to fit the data available to the various adsorption isotherms. The adsorption of the *Khillah* on the zinc metal surface obeyed Langmuir adsorption isotherm (Fig. 2) (R$^2$ is nearly to unity), The Langmuir adsorption model postulates that there is no interaction between the adsorbed molecules and the energy of adsorption is independent on the surface coverage

(Ө) and maximum adsorption corresponds to the saturated monolayer of Langmuir equation can be described by equation (3) [29, 30].

C/Ө = 1/K + C               (3)

The negative value of ΔG°$_{ads}$ for Langmuir -29.5 kJ mol$^{-1}$ indicate that *Khillah* extract is spontaneously adsorbed on the metal surface [31] and the adsorption mechanism is a combination of both physisorption and chemisorption (comprehensive adsorption) [32].
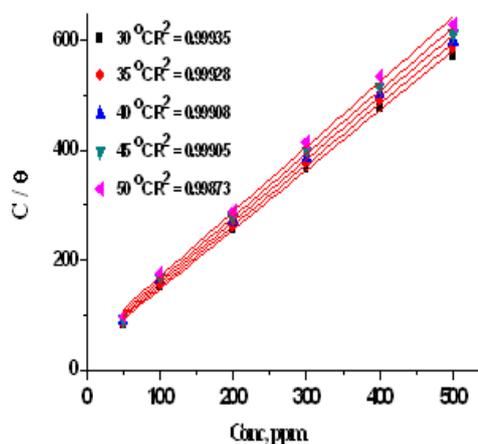


**Figure 2. Langmuir adsorption isotherm plotted as C/Ө vs .C of Khillah extract for the corrosion of Zn in 3.5 % NaCl and 16 ppm Na$_2$S solution at different temperatures**

## Effect of temperature

The effect of temperature on the % IE of the *Khillah* inhibitor was determined by weight loss method at different concentrations and at different temperatures (30-50°C) for a fixed immersion time of 180 min was shown in Figure 3. The data in Table 2 revealed that the inhibition efficiency decreased by increasing the temperature, due to desorption of adsorbed inhibitor components on Zn surface. This indicates that the extract components are mainly physically adsorbed on the metal surface.
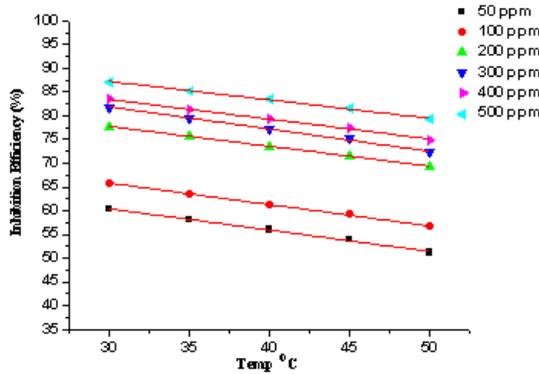


**Figure 3. Effect of temperature on the inhibition efficiencies of different concenteration of Khillah extract for the corrosion of Zn in 3.5 % NaCl and 16 ppm Na$_2$S at 30 – 50$^o$C**

**Thermodynamic parameters**

The activation energy (E$^*_a$), the entropy of activation (ΔS$^*$) and s the enthalpy of activation (ΔH$^*$) values are important to investigate the kinetics of the corrosion process. The apparent (E$^*_a$), (ΔS$^*$) and (ΔH$^*$) of metal corrosion in corrosive media can be calculated from the Arrhenius equation [33].

$$\ln k = (E^*_a)/RT + A \qquad (4)$$
$$k = RT/ Nh \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \qquad (5)$$

Where k is the corrosion rate, R is the universal gas constant, A is Arrhenius pre exponential factor, T is the absolute temperature, h is Planck's constant and N is Avogadro's number. The values of the activation energies, E$_a^*$, were calculated from Figure 4 and the values of ΔH$^*$ and ΔS$^*$ were calculated from Figure 5, [34]. The calculated values of the apparent activation energy, E$_a^*$, activation enthalpies, ΔH$^*$ and activation entropies, ΔS$^*$ are given in Table 3 which reported the increase in the activation energy indicating a strong adsorption of the inhibitor molecules on Zn surface and indicates the energy barrier caused by the adsorption of the *Khillah* molecules on Zn surface. The high value of E$_a^*$ in presence of *khillah* extract compared to that in its absence and the decrease in the % IE with rise in temperature is interpreted as indication of physical adsorption process [35–37]. The increase in the activation enthalpy (ΔH$^*$) in presence of the extract implies that the addition of the extract to the 3.5 % NaCl and 16 ppm Na$_2$S solution increases the height of the energy. barrier of the corrosion reaction to an extent depends on the type and concentration of the present inhibitor. The positive values of ΔH$^*$ reflect the endothermic nature of the corrosion process. Also the lower ΔH$^*$ values indicate that the inhibited corrosion reaction of zinc is supporting the proposed physisorption mechanism [32]. The entropy of activation (ΔS$^*$) in the blank and inhibited solutions is large and negative indicating that the extract molecules in the bulk solution are adsorbed in an orderly fashion onto the zinc surface resulting in a decrease in entropy. This implies that, the activated complex in the rate determining step represents association rather than

dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. [38-41].
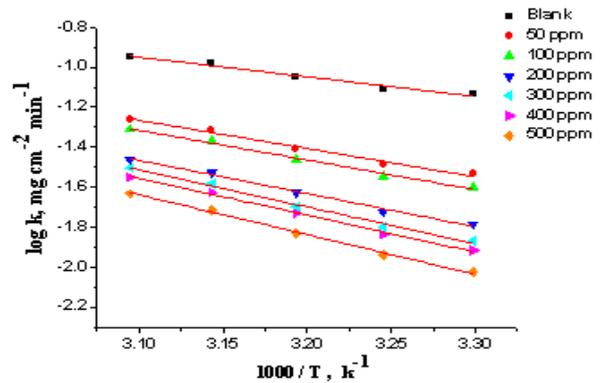


**Figure 4. Arrhenius plots (log k vs.1000/T) for Zn in 3.5 % NaCl and 16 ppm Na$_2$S in the absence and presence of different concentrations of Khillah extract**
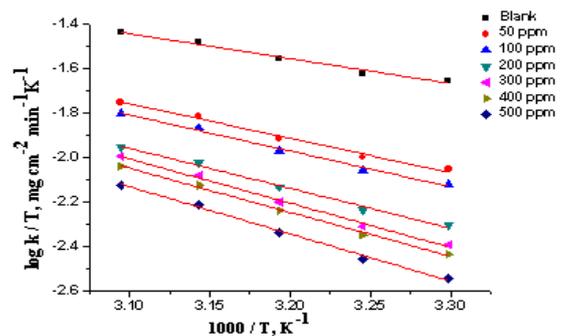


**Figure 5. Arrhenius plots (log k/T vs.1/T) for Zn in3.5% NaCl and 16 ppm Na$_2$S in the absence and presence of different concentrations of Khillah extract**

**Electrochemical measurements**

**Potentiodynamic polarization measurements**

The potentiodynamic polarisation curves of Zn in 3.5 % NaCl and 16 ppm Na$_2$S solution without and with various concentrations of *Khillah* extract is illustrated in Figure 6 Electrochemical corrosion kinetic parameters obtained by Tafel extrapolation method are given in Table 4. No definite shift in the corrosion potential (E$_{corr}$) is detected, although there was no specific relation between E$_{corr}$ and inhibitor concentration. It can be seen from Figure 6, that the cathodic and anodic reactions are affected by the presence of the extract indicating that *Khillah* extract acts as mixed-type inhibitor. It can be seen from the polarization results that the corrosion current density (i$_{corr}$) decreased with the increase in extract concentration, due to the increase in the blocked fraction of the metal surface by adsorption.
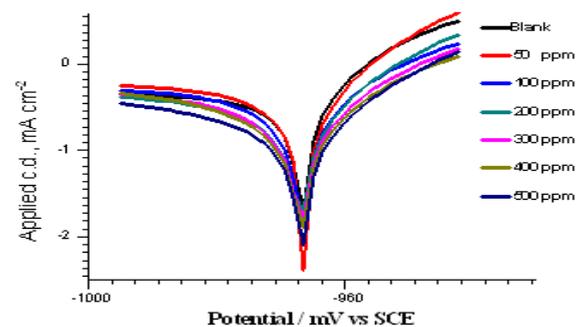


**Figure 6. potentiodynamic polarization curve for zinc corrosion in 3.5% NaCl and 16 ppm Na$_2$S in the absence and presence of different concentrations of Khillah extract at 30$^o$C**

**Electrochemical impedance spectroscopy (EIS) method**

Electrochemical impedance spectroscopy (EIS)have been shown to be an efficient and convincing tool for analyzing the corrosion behavior of metals. Impedance diagram Nyquist plot obtained for Zn in absence and the presence of various concentrations of the *Khillah* extract in 3.5 % NaCl and 16 ppm Na$_2$S solution is depicted in Figure (7). As a result, the semicircle in the presence of extract is bigger than that in the absence of extract (Blank) and increases as the extract concentration increases. This confirms that the impedance of inhibited Zn substrate increases with the concentration of *Khillah* extract. The electrochemical impedance parameters were calculated from the Nyquist plots and are given in Table 5. Values of charge transfer resistance (R$_{ct}$)**,** % IE increase and double layer capacitance (C$_{dl}$) decrease with increasing extract concentration. This is attributed to high resistance shown by the adsorbed extract components at the metal − solution interface and increase in thickness of electrical double layer due to adsorption of extract components. On the other hand, the values of C$_{dl}$ are decreased with increase in inhibitor concentration which is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer, suggests that the extract acts via adsorption at the metal/solution interface [42, 43]. It could be assumed that the decrease of C$_{dl}$ values is caused by the gradual replacement of water molecules by adsorption of organic molecules on the electrode surface, which decreases the extent of the metal dissolution. The equivalent circuit depicted in Figure 8 is employed to analyze the impedance spectra for *Khillah*.
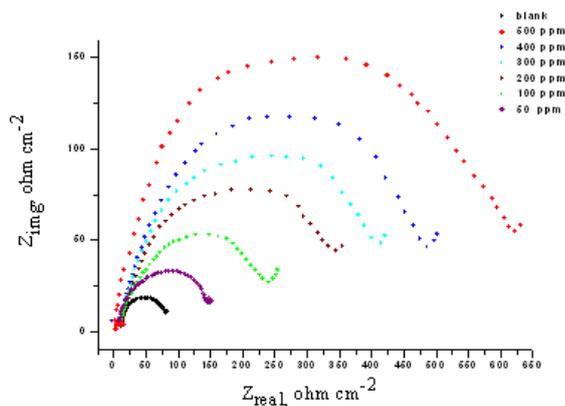


**Figure 7. Nyquist plots for Zn corrosion in 3.5% and 16 ppm Na$_2$S solution in the absence and presence of different concentrations of Khillah at 30ºC**
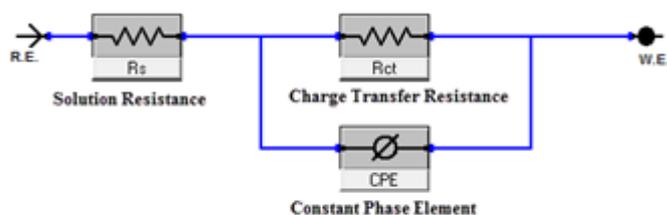


**Figure 8. Equivalent circuit model used to fit experimental EIS data**

**Electrochemical frequency modulation (EFM) method**

The EFM is a non destructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants [44, 45]. Figure 9 shows the intermodulation spectra obtained from EFM measurements of zinc corrosion in 3.5 % NaCl and 16 ppm Na$_2$S solution in the absence of the investigated *Khillah* extract, and

Figure 10 shows the intermodulation spectra obtained from EFM measurements of zinc corrosion in 3.5 % NaCl and 16 ppm Na$_2$S solution in presence of 500 ppm *Khillah* extract. The calculated corrosion kinetic parameters at different concentrations of the *Khillah* in 3.5 % NaCl and 16 ppm Na$_2$S at 30ºC is given in Table 6. From this Table, the corrosion current density decreases and the inhibition efficiency increases by increasing the concentration of investigated extract. The great strength of the EFM is the causality factor, which serves as an internal check on the validity of the EFM measurement [46]. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. The deviation of causality factors from their ideal values might due to that the perturbation amplitude was too small or that the resolution of the frequency spectrum is not high enough.
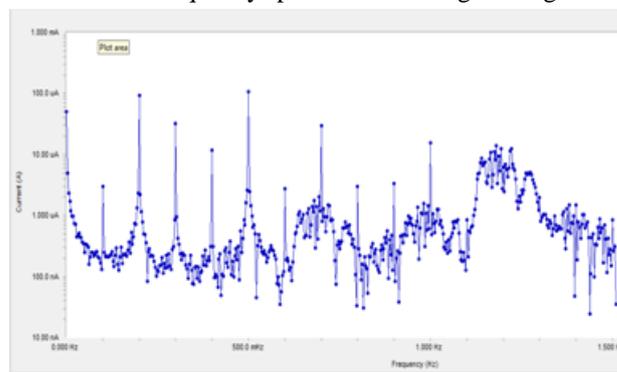


**Figure 9. EFM spectra obtained for zinc corrosion in 3.5 % NaCl and 16 ppm Na$_2$S solution in the absence of Khillah at 25 ºC**
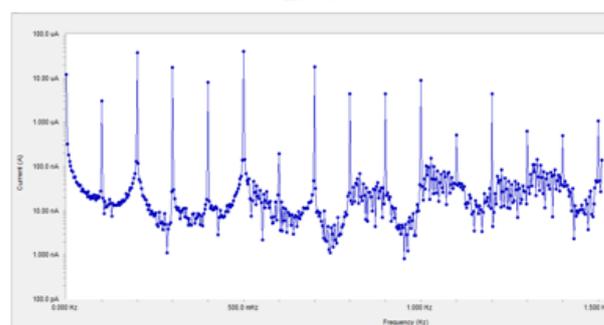


**Figure 10. EFM spectra obtained for zinc corrosion in 3.5 % NaCl and 16 ppm Na$_2$S solution in the presence of 500 ppm of Khillah at 25 ºC**

**Mechanism of corrosion inhibition**

Organic compounds containing π- electrons, hetero atoms and multiple bonds have been reported to function as effective inhibitors for the corrosion of many metals in various media [47, 49]. When immersed zinc in a neutral aqueous environment, the anodic reaction is:

$$Zn \rightleftharpoons Zn^{2+} + 2e^- \qquad (6)$$
$$Zn^{2+} + 2Cl^- \rightleftharpoons ZnCl_2 \qquad (7)$$
$$Zn^{2+} + S^{2-} \rightleftharpoons ZnS \qquad (8)$$

The cathodic reaction is:
$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad (9)$$
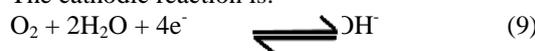
The khillah extract components can adsorb on the Zn surface via the lone pairs of electrons present on their oxygen atoms and the π-electrons of the benzene rings. The adsorption of such compounds on the metal surface make a barrier for charge and mass transfer leading to decrease the interaction of the metal with the corrosive environment. As a result, the corrosion rate of the metal is decreased.

| Element | Pb | Fe | Cd | Cu | Zn |
|---|---|---|---|---|---|
| weight% | 0.001 | 0.002 | 0.001 | 0.003 | Rest |

**Table 1. Data from weight loss of zinc dissolution in 3.5 % NaCl and 16 ppm $Na_2S$ solution containing different concentrations of Khillah extract after 180 min immersion at $30^oC$**

| Khillah Conc,ppm | 50 | 100 | 200 | 300 | 400 | 500 |
|---|---|---|---|---|---|---|
| % IE | 60.3 | 65.8 | 77.7 | 81.7 | 83.4 | 87.2 |

**Table 2. The effect of temperature on the % IE of the Khillah extract at different concentrations and at different temperatures ($30-50°C$) after 180 min immersion**

| Khillah Conc, ppm | | | | | | |
|---|---|---|---|---|---|---|
| Temp $^oC$ | 50 | 100 | 200 | 300 | 400 | 500 |
| | % IE | | | | | |
| 30 | 60.3 | 65.8 | 77.7 | 81.7 | 83.4 | 87.1 |
| 35 | 58.1 | 63.4 | 75.6 | 79.5 | 81.2 | 85.3 |
| 40 | 56.0 | 61.2 | 73.4 | 77.2 | 79.2 | 83.4 |
| 45 | 53.8 | 59.2 | 71.5 | 75.1 | 77.4 | 81.4 |
| 50 | 51.2 | 56.5 | 69.3 | 72.2 | 74.9 | 79.3 |

**Table 3. Activation parameters for dissolution of Zn in absence and presence of different concentrations of Khillah extract in 3.5 % NaCl and 16 ppm $Na_2S$**

| Extract | Conc.,ppm | Activation parameters | | |
|---|---|---|---|---|
| | | $E_a^*$ | $\Delta H^*$ | $-\Delta S^*$ |
| Blank | 3.5 % NaCl + 16 ppm $Na_2S$ | 21.4 | 9.3 | 158.7 |
| Khillah | 50 | 29.7 | 12.9 | 139.0 |
| | 100 | 30.9 | 13.4 | 136.1 |
| | 200 | 34.4 | 14.9 | 128.2 |
| | 300 | 38.2 | 16.6 | 117.4 |
| | 400 | 38.8 | 16.8 | 115.2 |
| | 500 | 40.7 | 17.6 | 112.0 |

**Table 4. Corrosion parameters of Zn electrode in 3.5 % NaCl and 16 ppm $Na_2S$ solution in the absence and presence different concentrations of Khillah extract at $30^oC$**

| Conc, ppm | $-E_{corr}$ mV vs SCE | $i_{corr}$ $\mu A$ $cm^{-2}$ | Tafel slop | | $R_p$ $\Omega$ $cm^2$ | Ɵ | %IE |
|---|---|---|---|---|---|---|---|
| | | | $\beta_a$ $mVdec^{-1}$ | $\beta_c$ $mVdec^{-1}$ | | | |
| Blank | 964 | 731.9 | 173 | 34 | 29.12 | -- | -- |
| 50 | 964 | 299.1 | 118 | 29 | 72.14 | 0.598 | 59.8 |
| 100 | 964 | 253.3 | 84 | 28 | 84.68 | 0.653 | 65.3 |
| 200 | 964 | 171.1 | 70 | 27 | 125.61 | 0.766 | 76.6 |
| 300 | 964 | 142.3 | 61 | 25 | 152.92 | 0.805 | 80.5 |
| 400 | 964 | 123.3 | 33 | 24 | 171.92 | 0.831 | 83.1 |
| 500 | 964 | 96.4 | 29 | 22 | 212.15 | 0.868 | 86.8 |

**Table 5. Impedance parameters and inhibition efficiency for zinc corrosion in 3.5 % NaCl and 16 ppm $Na_2S$ solution in the absence and presence of different concentrations of Khillah at $30^oC$**

| Conce, ppm | $R_{ct}$, ohm $cm^2$ | $C_{dl, x}$ $\mu F$ $cm^{-2}$ | Ɵ | %IE |
|---|---|---|---|---|
| Blank | 82.37 | $1.8 \times 10^{-5}$ | -- | --- |
| 50 | 207.70 | $0.74 \times 10^{-5}$ | 0.603 | 60.3 |
| 100 | 240.60 | $0.66 \times 10^{-5}$ | 0.658 | 65.8 |
| 200 | 354.30 | $0.59 \times 10^{-5}$ | 0.768 | 76.8 |
| 300 | 415.50 | $0.45 \times 10^{-5}$ | 0.807 | 80.7 |
| 400 | 487.40 | $0.34 \times 10^{-5}$ | 0.831 | 83.1 |
| 500 | 625.60 | $0.21 \times 10^{-5}$ | 0.868 | 86.8 |

**Table 6. EFM spectra of zinc corrosion in 3.5 % NaCl and 16 ppm $Na_2S$ solution in the absence and presence of different concenteration of Khillah at $30^oC$**

| Conc, ppm | $i_{corr.}$ $\mu A$ $cm^{-2}$ | $\beta_a$ $mVdec^{-1}$ | $-\beta_c$ $mVdec^{-1}$ | C.R mpy | CF2 | CF3 | Ɵ | % IE |
|---|---|---|---|---|---|---|---|---|
| Blank | 331.5 | 71 | 203 | 305.5 | 2.249 | 2.161 | -- | -- |
| 50 | 135.6 | 57 | 489 | 125.5 | 2.188 | 2.387 | 0.591 | 59.1 |
| 100 | 115.7 | 50 | 281 | 90.6 | 2.076 | 4.959 | 0.651 | 65.1 |
| 200 | 78.2 | 44 | 282 | 62.85 | 2.096 | 5.448 | 0.764 | 76.4 |
| 300 | 68.2 | 41 | 392 | 53.44 | 2.098 | 5.916 | 0.794 | 79.4 |
| 400 | 55.2 | 36 | 194 | 48.33 | 2.075 | 6.308 | 0.834 | 83.4 |
| 500 | 40.6 | 33 | 126 | 37.42 | 2.065 | 6.424 | 0.877 | 87.7 |

Inspection of Figure 12 reveals that both khellin and visnagin molecules have structure characterized by the presence of chelation center represented by the two adjacent methoxy groups. Such structure facilitates the formation of a complex with the dissolved zinc ions. The formation of insoluble complex on the metal surface isolates the metal from the aggressive solution and therefore inhibits the corrosion process.
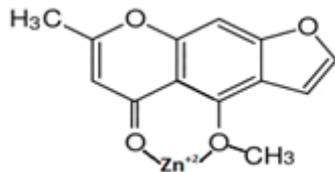


**Figure 12. Structure formulas of the formed complex compounds**

## Conclusions

The khillah extract acts a good corrosion inhibitor for zinc in 3.5% NaCl and 16 ppm $Na_2S$ solution. The inhibition action of the extract was attributed to the presence of furanochromones (khellin and visnagin) which adsorbed on Zn surface. The inhibition efficiency decreased as the temperature increased. The adsorption follows Langmuir adsorption isotherm. The adsorbed species formed insoluble complex compounds upon their interaction with the dissolved zinc ions. All examined methods gave approximately similar results of % IE, indicating good agreements between these different methods.

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