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Khillah extract as inhibitor for acid corrosion of SX 316 steel

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Abstract

The inhibitive effect of the extract of khillah (*Ammi visnaga*) seeds, on the corrosion of SX 316 steel in HCl solution was determined using weight loss measurements as well as potentiostatic technique. It was found that the presence of the extract reduces markedly the corrosion rate of steel in the acid solution. The inhibition efficiency increases as the extract concentration is increased. The inhibitive effect of khillah extract was discussed on the basis of adsorption of its components on the metal surface. Negative values were calculated for the energy of adsorption indicating the spontaneity of the adsorption process. The formation of insoluble complexes as a result of interaction between iron cations and khellin, which present in the extract, was also discussed.

Keywords: Acid inhibition; Natural product; Khillah; Steel 316

1. Introduction

SX 316 is an improved version of SX 304, with the addition of molybdenum and slightly higher nickel content. The resultant composition of SX 316 gives the steel much increased corrosion resistance in many aggressive environments. The molybdenum makes the steel more resistant to pitting and crevice corrosion in chloride-contaminated media. The lower rate of general corrosion in mildly corrosive environments gives the steel good atmospheric corrosion resistance in polluted marine atmospheres.

Because of its superior corrosion and oxidation resistance, good mechanical properties and fabricability, SX 316 has applications in many sectors of industry include tanks and storage vessels for corrosive liquids. Specialised process equipment in the chemical, food, paper, mining, pharmaceutical and petroleum industries.

Nevertheless, SX 316 steel could be attacked by highly concentrated acids during the cleaning and pickling process. Therefore, the presence of corrosion inhibitors in the cleaning and pickling solutions is very important to keep the surface of steel intact. For this reason, many researches were conducted to study its corrosion properties and to find out suitable chemical compounds to be used as corrosion inhibitors for it in acidic solutions [1–8]. However, most of used compounds are dangerous for human and environment. Recently, there were several researches concerning the use of naturally occurring substances as corrosion inhibitors for several metals in different media [9–17]. The use of such green compounds will add to the efforts which recently activated to protect our planet from the used harmful chemicals.

In this work, the extract of khillah seeds was tested as corrosion inhibitor for general corrosion of SX 316 steel in hydrochloric acid. Khillah or Bishop's Flower (*Ammi visnaga*) is an annual plant belongs to family Umbelliferae. It is cultivated in many areas in the world such as Europe, Asia and Africa. The aqueous extraction of its seeds is used for treatment of several diseases without side effects [18].

2. Experimental methods

SX 316 steel with the composition shown in Table 1 was used. Coupons with exposed surface area of 25 cm^2 (2 cm × 5.6 cm × 0.2 cm) were used for weight loss measurements. For potentiostatic studies, a cylindrical rod embedded in araldite with exposed surface area of 0.16 cm^2, was used. The electrodes were polished with 1/0 to 4/0 grades of emery papers, degreased with acetone and rinsed by distilled water, before inserted in the test solution.

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Table 1
Chemical composition of SX 316 steel

C	0.08
Mn	2.0
P	0.045
S	0.030
Si	1.0
Cr	16.0
Ni	10.0
Mo	2.00

For weight loss measurements, the steel coupons were left hanged in the test solution (2.0 M HCl) for 10 days at 25 ± 1 °C before recording the loss of their weights. The corrosion rate was calculated on the basis of the apparent surface area. The inhibition efficiencies calculations were based on the weight loss measurements at the end of the whole exposure period. The results of the weight loss experiments are the mean of three runs, each with a fresh sheet and fresh electrolyte. The percent of inhibition efficiency was calculated using the following equation:

$$IE = \left[\frac{CR_f - CR_i}{CR_f}\right] \times 100 \quad (1)$$

where CR_f and CR_i are the corrosion rates of the steel coupons, in absence and presence of khillah extract, respectively.

Potentiostatic polarization studies were carried out using a (PS remot) potentiostat with zum PS6 software for calculation of corrosion parameters. The potential was scanned at a rate of 5.0 mV s^{-1}. Three-compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. The inhibition efficiency IE was calculated using the following equation:

$$IE = \left[\frac{I - I_i}{I}\right] \times 100 \quad (2)$$

where I and I_i are the corrosion rates in free and inhibited acid, respectively.

Conductometric titration was applied by titrating a solution of 10^{-3} M $FeCl_2$ in a solution of 10^{-4} M khellin. After the addition of the titrant the solution is mechanically stirred to attain equilibrium and the conductance of the solution is measured.

All chemicals used for preparing the test solutions were of analytical grade. The basic experiments (other than those carried out at different temperatures) were carried out at room temperature, 25 ± 1 °C.

The seeds of khillah were crushed and extracted in aqueous medium by steam distillation for 2 h. The extracted solution was then filtered, concentrated by evaporation on steam bath until it become 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. Pure khellin from Sigma–Aldrich was used in the experiments.

3. Results and discussion

3.1. Weight loss measurements

Table 2 contains the rate of corrosion of SX 316 steel in 2.0 M HCl solutions devoid of and containing different concentrations of khillah extract. The rate of corrosion was tabulated as grams per square meter per day (g m^{-2} d^{-1}) and the concentration of extract was expressed as part per million (ppm) as well as equivalent molar (mol dm^{-3}) of khellin. For comparison, the same concentrations of pure khellin were used in separate experiments and the results were given also in Table 2. Due to the low solubility product of khellin ($\sim 9.7 \times 10^{-4}$ M), only five concentrations of it were tested, as shown in the table.

Inspection of Table 2 reveals that the corrosion rate of steel is highly reduced upon addition of khillah extract. This result indicates that khillah extract acts as good inhibitor for acid corrosion of SX 316 steel. The values of inhibition efficiencies of different khillah extract concentrations are given in Table 2. As revealed from the data in Table 2, khillah extract has quite high inhibition efficiency that reaches up to 99.3% for 300 ppm of the added extract. The inhibition efficiency increased as the concentration of extract was increased.

Khillah seed contains small amount of volatile fatty oil, coumarins and furanochromones such as khellin and visnagin [19]. Among these compounds, the furanochromones have the highest concentrations in the aqueous extract of the seeds. Khillah seeds contain 10,000–40,000 ppm of furanochromones, most of them is khellin [20]. These compounds are responsible for the treatment of many diseases. The data of

Table 2
Weight loss data of SX 316 steel in free and inhibited acid solutions

Extract concentration		Corrosion rate (g m^{-2} d^{-1})	IE (%)	Khellin concentration (mol dm^{-3})	Corrosion rate (g m^{-2} d^{-1})	IE (%)
ppm	As molar khellin					
0.00	0.00	0.288	–	0.00	0.288	–
30	0.00011	0.081	71.87	0.00011	0.091	68.40
60	0.00023	0.051	82.29	0.00023	0.052	81.94
120	0.00046	0.012	95.83	0.00046	0.028	90.27
180	0.00069	0.011	96.18	0.00069	0.016	94.44
240	0.00092	0.008	97.22	0.00092	0.012	95.83
300	0.00115	0.004	99.30	–	–	–

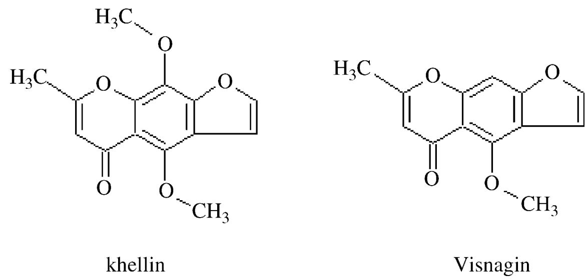

Fig. 1. Chemical formulas of khellin and visnagin.

Table 2 reveals that the inhibition efficiencies obtained by addition of different extract concentrations are comparable with those obtained by the same concentrations of khellin. This result suggests that khellin is responsible for the inhibitive action of khillah extract.

The chemical formula of khellin and visnagin are represented in Fig. 1. Inspection of the chemical structures of furanochromones reveals that these compounds can adsorb on the metal surface via the lone pairs of electrons present on their oxygen atoms. 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.

3.2. Potentiostatic polarization

Fig. 2 represents the anodic and cathodic polarization curves of SX 316 steel in 2.0 M HCl solutions devoid of and containing different concentrations of khillah extract. Inspection of the figure reveals that the polarization curves shift toward less negative potential and lower current density values upon the addition of the extract. This behaviour reflects the inhibitive action of khillah extract. The corrosion parameters of SX 316 steel in the free and inhibited acid solutions were obtained from the curves of Fig. 2 and given in Table 3. The data in Table 3 show that the corrosion potential shifts to less negative values as the concentration of added extract is increased. On the other hand, the corrosion current density is markedly decreased upon addition of the extract. The extent of its decrease increases with increased extract concentration. Moreover, the numerical values of both anodic and cathodic Tafel constants decreased as the concentration of extract was increased.

3.3. Adsorption behaviour

To study the adsorption behaviour of furanochromones on steel surface in the given medium, the adsorption isotherm must be defined. Therefore, the relation between the concentration of extract (C) and the fraction of steel surface covered by the adsorbed compounds (θ) was obtained. Because the inhibition action is postulated as a result of the adsorption process (θ), is directly related with the inhibition efficiency (IE) and was calculated using the equation: $\theta = \mathrm{IE}/100$. The best fit was obtained for the relation between (C/θ) and C, which represented in Fig. 3. A straight line was obtained with almost unity slope indicating that the adsorption process follows Langmuir adsorption isotherm. This isotherm postulates that there is no interaction between the adsorbed molecules and the energy of adsorption is independent on the surface coverage (θ). Langmuir adsorption isotherm could be represented using the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{3}$$

where K is the adsorption constant and

$$\ln K = \ln\frac{1}{55.5} - \frac{\Delta G^{\circ}_{\mathrm{ad}}}{RT} \tag{4}$$

The standard free energies for adsorption were calculated using Eq. (4) where one molecule of water is replaced by one molecule of inhibitor [21]. The numerical value (1/55.5) in Eq. (4) stands for molarity of water. The value of $\Delta G^{\circ}_{\mathrm{ad}}$ for adsorption of extract components (calculated as khellin) was found to be -34.5 kJ mol^{-1}. The negative sign of free energy of adsorption indicates that the adsorption of khillah extract at steel surface is a spontaneous process.

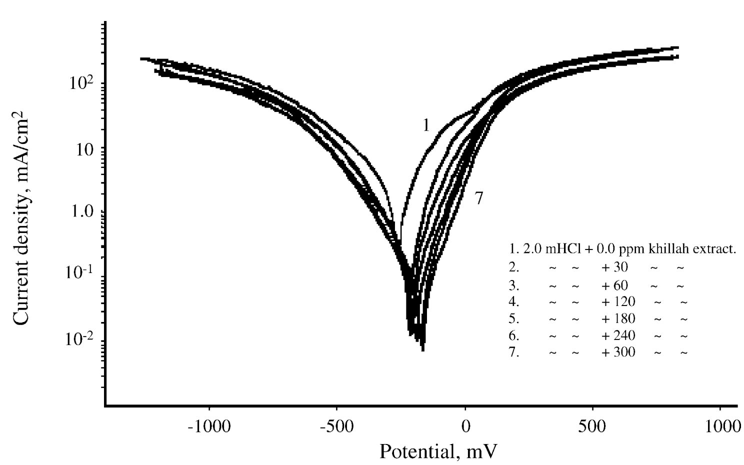

Fig. 2. Polarization curves of SX 316 steel in free and inhibited acid solutions.

Table 3
Corrosion parameters of SX 316 steel in free and inhibited 2.0 M HCl solutions

Extract concentration		$-E_{corr}$ (mV)	I_{corr} (mA/cm^2)	β_a (mV/dec.)	$-\beta_c$ (mV/dec.)	IE (%)	θ
ppm	As molar khellin						
0.0	0.0	225	1.16	115	271	–	–
30	0.00011	219	0.34	94	223	70.69	0.707
60	0.00023	208	0.21	92	207	81.89	0.819
120	0.00046	192	0.06	91	154	94.82	0.948
180	0.00069	186	0.05	91	147	95.69	0.957
240	0.00092	160	0.04	87	142	96.55	0.966
300	0.00115	159	0.02	75	117	98.27	0.982

3.4. Effect of temperature

The effect of temperature on the corrosion parameters of SX 316 steel in free and inhibited solutions of 2.0 M HCl was studied using polarization technique in temperature range 40–80 °C. The acid solutions were inhibited by addition of 120 ppm of khillah extract. The variation of temperature has no effect on the general shape of the polarization curves (not shown). The obtained corrosion parameters are given in Table 4. Inspection of Table 4 reveals that the corrosion rate of steel increases with increased temperature. On the other hand, the inhibition efficiency of khillah extract decreases as the temperature was increased. The activation energy of corrosion process in free and inhibited acid could be calculated using the equation:

$$K = A\exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where E_a is the activation energy, A the frequency factor, T the absolute temperature, R the gas constant and K is the rate of corrosion reaction, which is directly proportion with the corrosion current density. Fig. 4 represents the relationship between $\log K$ and $\frac{1}{T}$. The values of activation energy calculated using the curves of Fig. 4 are 26.95 and 41.04 kJ mol^{-1} for free and inhibited acid solutions, respectively. The obtained results suggest that khillah extract inhibits the corrosion reaction by

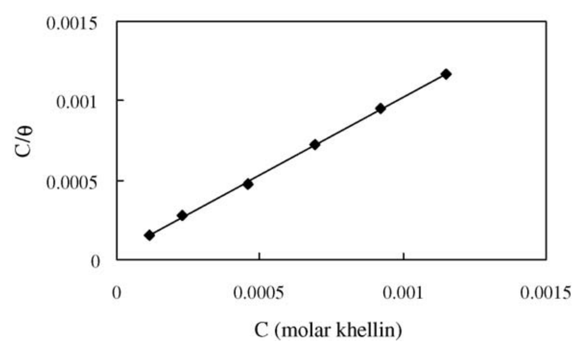

Fig. 3. Adsorption isotherm of khillah extract at steel surface.

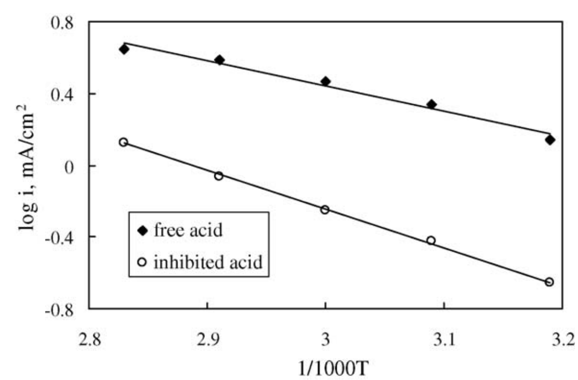

Fig. 4. Relationship between temperature and corrosion current density.

Table 4
Effect of temperature on the inhibition efficiency of 120 ppm khillah extract

2.0 M HCl	$-E_{corr}$ (mV)	I_{corr} (mA/cm^2)	IE (%)	θ
40 °C	192	1.38	–	–
Inhibited	170	0.15	89.13	0.8913
50 °C	181	2.18	–	–
Inhibited	164	0.31	85.78	0.8578
60 °C	175	2.91	–	–
Inhibited	126	0.56	80.75	0.8075
70 °C	175	3.83	–	–
Inhibited	131	0.89	76.76	0.7676
80 °C	175	4.44	–	–
Inhibited	120	1.3	70.72	0.7072

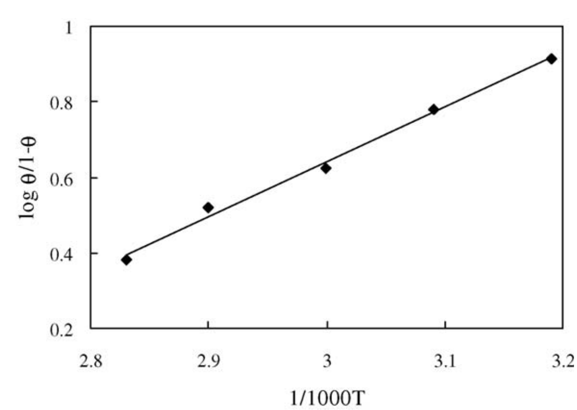

Fig. 5. Relationship between temperature and surface coverage.

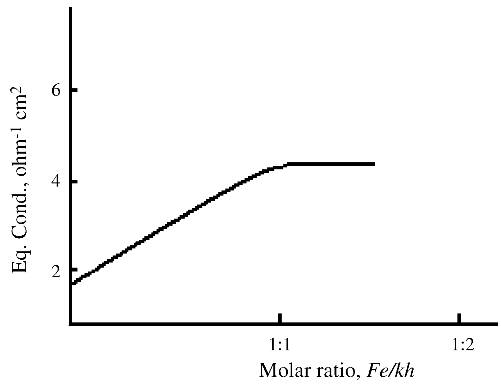

Fig. 6. Conductance–molar ratio curve for Fe–khellin. Eq. Cond. (equivalent conductance) and Fe/kh (iron/khellin).

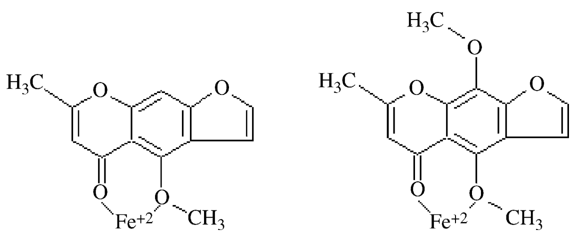

Fig. 7. Structure formulas of the formed complex compounds.

increasing its activation energy. This could be done by adsorption on the steel surface making a barrier for mass and charge transfer. However, such types of inhibitors perform a good inhibition at ordinary temperature with considerable loss in inhibition efficiency at elevated temperatures [22]. Moreover, the high value of activation energy in presence of khillah extract suggests a chemical adsorption process.

Langmuir adsorption isotherm may be represented by [23]:

$$\log\frac{\theta}{1-\theta} = \log A + \log C - \frac{\Delta H}{2.303RT} \quad (6)$$

where ΔH is heat of adsorption. Therefore, plotting $\log\frac{\theta}{1-\theta}$ versus $\frac{1}{T}$ give straight line (Fig. 5) with a slope equals to $-\frac{\Delta H}{2.303R}$. It was found that the heat of adsorption of khillah extract (calculated as khellin) is -27.75 kJ mol^{-1}. The negative value of the heat of adsorption indicates that the adsorption process is exothermic.

3.5. Inhibition mechanism

Inspection of Fig. 1 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 iron ions. A conductometric titration was carried out using solutions of $FeCl_2$ and khellin in acidic medium. The obtained conductance–molar ratio curve (Fig. 6) is characterized by one break. The position of this break give indication about the formation and composition of the complex formed in the solution. This result confirmed the formation of an insoluble 1:1 complex compound. The chemical formulas of the formed complex compounds are represented in Fig. 7. The formation of insoluble complex on the metal surface isolates the metal from the aggressive solution and therefore inhibits the corrosion process.

4. Conclusions

- Khillah extract acts as good inhibitor for SX 316 steel in HCl solution.
- The inhibition action of the extract was attributed to the presence of furanochromones (khellin and visnagin).
- The inhibition efficiency decreased as the temperature was increased.
- Inhibition effect was performed via the adsorption of furanochromones on the steel surface. The adsorption follows Langmuir adsorption isotherm.
- The adsorbed species formed insoluble complex compounds upon their interaction with the dissolved iron ions..

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