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Control of zinc corrosion in acidic media: Green fenugreek inhibitor

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Abstract: Fenugreek seeds extract was examined as a green corrosion inhibitor for Zn in 2.0 mol/L H_2SO_4 and 2.0 mol/L HCl solutions by mass loss and electrochemical measurements. Scanning electron microscope (SEM) images show that the surface damage is decreased in the presence of the inhibitor. X-rays photoelectron spectroscopy (XPS) analysis was performed to identify the corrosion product, ZnO, and to prove the inhibitor adsorption mechanism. The maximum inhibition efficiency values are 90.7% after 1 h and 66.6% after 0.5 h by 200 mL/L of fenugreek extract in H_2SO_4 and HCl solutions, respectively. Addition of I^- ion greatly improves the inhibition efficiency of fenugreek seeds extract for Zn corrosion in HCl due to the synergistic effect. Potentiodynamic polarization and EIS measurements prove the inhibition ability of fenugreek for Zn corrosion in HCl as indicated by the decreased corrosion current density and increased charge transfer resistance values in the presence of fenugreek.

Key words: zinc; corrosion mechanism; inhibitor; synergetic effect

1 Introduction

Due to environmental regulations, plant extracts have again become important as they are environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. A lot of natural products were previously reported as green corrosion inhibitors for Zn in various environments such as aloe vera extract [1], citrullus vulgaris peel [2], mansoa alliacea plant extract [3], moringa oleifera extract [4], red onion skin acetone extract [5], and thiourea [6]. The corrosion rate was determined by mass loss measurements [1,2,4−6], polarization [3,4] and electrochemical impedance spectroscopy [4]. It was found that the inhibition efficiency increased with increasing concentration of the extract but decreased with increasing temperature [1,2,4,5]. The adsorption of the inhibitor molecules on Zn surface was in accordance with Langmuir [1,2,6] or Temkin [2,4] adsorption isotherms. Thermodynamic parameters such as heat of adsorption and free energy of adsorption suggested that the adsorption of inhibitor on the Zn metal surface is exothermic and followed by spontaneous process [1,2,4,6]. Potentiodynamic polarization curves indicated that the plant extract [3,4] behaves as mixed-type inhibitor and retards the anodic and cathodic corrosion reactions. The inhibition efficiency values were found to be 67.1% [1] and 68% [5] and 59.8% [6] in 2.0 mol/L HCl solution, 72.7% in natural sea water [2], 88.4% [4] and 92.0% in 3% NaCl solution [3].

The effect of aqueous extract of fenugreek leaves and seeds on the corrosion of mild steel in HCl and H_2SO_4 solutions was investigated [7]. Seeds inhibit mild steel corrosion more than leaves, and the inhibition efficiency is always greater in HCl (82.4% and 84.9%) than in H_2SO_4 (65.8% and 63.7%) solutions, respectively. In HCl solution, the adsorption of fenugreek inhibitor on mild steel surface obeys the Langmuir adsorption isotherm in HCl solution, while obeys the Temkin adsorption isotherm in H_2SO_4 solution. AGARWAL [8] reported the inhibitive action of the extracts of lemon peel and fenugreek leaves on the corrosion of mild steel in HCl solution. The adsorption of lemon peel and fenugreek leave extracts on the mild steel surface in HCl solution obeys the Langmuir adsorption isotherm model and the adsorption is physical and spontaneous. The maximum inhibition efficiency is 85.2 % by using 50 mL/L of the extract. On the other hand, synergism has

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been reported for zinc corrosion only in alkaline media [9−11].

In the present work, the inhibition ability of fenugreek extract for Zn corrosion in 2.0 mol/L H_2SO_4 and HCl solutions is investigated by mass loss and electrochemical methods. Several factors are studied such as immersion time, inhibitor concentration and temperature, to identify best conditions for the inhibition performance of fenugreek. The proper adsorption isotherm is identified and important thermodynamics parameters are calculated. Furthermore, a possible improvement of the fenugrueek inhibition performance in HCl medium is presented.

2 Experimental

2.1 Materials

Zn (BDH grade) was used in this study with the following chemical composition: 0.001% lead, 0.002% iron, 0.001% cadmium, 0.003% copper and rest is Zn.

Zn specimens used have a cylindrical form (length, 6.3 mm; radius, 6.0 mm). Pre-treatment of specimens prior to experiments was carried out by polishing with series of a proper polishing paper (grade 180, 600 and 1500), rinsing with purified water, degreasing in acetone in an ultrasonic bath immersion for 5 min, washing again with purified water and then drying at room temperature before use.

The acid solutions (2.0 mol/L H_2SO_4 and 2.0 mol/L HCl) were prepared by dilution of 95%−97% H_2SO_4 (Sigma Aldrich) and 37% HCl (Sigma Aldrich), respectively with double-distilled water. KI (99.5% Sigma Aldrich) was used as received.

2.2 Preparation of fenugreek extracts

Commercial seeds of fenugreek were obtained (about 10 g), ground and boiled in distilled water for 1 h. The extract was left over night, then filtered and completed to 250 mL by distilled water [7].

2.3 Mass loss measurements

The gravimetric measurements were carried out using a sensitive balance (precision ±0.1 mg). After immersion period, Zn specimens were removed from the test solution, washed with distilled water, dried at room temperature and then reweighed. Experiments were carried out three times to ensure reproducibility and the mean value of the mass loss is calculated.

The corrosion rates (C_R) were calculated using Eq. (1):

$$C_R = \frac{KW}{DAt} \quad (1)$$

where C_R is corrosion rate in mils per year (mpy), W is mass loss in g, A is the specimen surface area in cm^2, t is the immersion period in h, D is density of zinc in gm/cm^3 and K is a constant equal to 3.45×10^6.

From the corrosion rate, the surface coverage (θ) as a result of adsorption of the extract components, and inhibition efficiencies of the plant extracts η were determined using Eqs. (2) and (3), respectively.

$$\theta = \frac{C_{R0} - C_{Ri}}{C_{R0}} \quad (2)$$

$$\eta = \frac{C_{R0} - C_{Ri}}{C_{R0}} \times 100\% \quad (3)$$

where C_{R0} and C_{Ri} are the corrosion rates in the absence and presence of the plant extracts, respectively.

2.4 Electrochemical measurements

Electrochemical measurements were carried out using a Solartron SI 1287 and frequency response analyzer 1252A system in a conventional three electrode-one compartment cell with Zn as the working electrode, 3.0 mol/L Ag/AgCl as a reference electrode, and a large surface area sheet of platinum as an auxiliary electrode. Potentiodynamic polarization was carried out by scanning the potential from −0.25 to 0.25 V versus open-circuit corrosion potential (OCP) at a scan rate of 1 mV/s. Electrochemical impedance spectroscopy (EIS) was measured at OCP in the frequency range from 100 kHz to 10 mHz under excitation of a sinusoidal wave of 5 mV amplitude. Before Tafel polarization and EIS experiments, the OCP of the working electrode was measured as a function of time during 5 min, the time needed to achieve a quasi-stationary value for the OCP.

2.5 Surface and structural characterization

Scanning electron microscopy (SEM) analysis was done by Quanta FEQ 250 with accelerating voltage of 30 kV.

XPS analysis was done by Thermo scientific K-Alpha XPS. A monochromatic Al K_α X-ray source was used for all the samples, along with pressure in the analysis chamber of 1×10^{-8} Pa. The resolution of the instrument has been found to have a width of 0.35 eV using silver Fermi edge. All spectra were analyzed using Avantage data software version 3.10 (Thermo Scientific Instruments)

3 Results and discussion

3.1 Surface characterization

The surface morphology of Zn was studied by SEM after being immersed in two corrosive media, H_2SO_4 and HCl for 1 and 0.5 h, respectively, in the absence (Figs. 1(a) and (c)) and presence (Figs. 1(b) and (d)) of

200 mL/L of the fenugreek seeds extract. Surface deterioration can be observed when immersing Zn in H_2SO_4 and HCl solutions, as shown in Figs. 1(a) and (c), respectively. This deterioration is largely decreased in the presence of the plant extract (Figs. 1(b) and (d)), indicating the inhibition ability of the fenugreek extract Zn corrosion in both acidic media.

3.2 Mass loss experiment: Immersion time effect

The variation of the mass loss of Zn with immersion time in 2.0 mol/L H_2SO_4 and 2.0 mol/L HCl solutions in the absence and presence of fenugreek extract at 28 °C is shown in Figs. 2(a) and (b), respectively. In general, mass loss is increased by increasing immersion time, however, in the presence of fenugreek extract, this

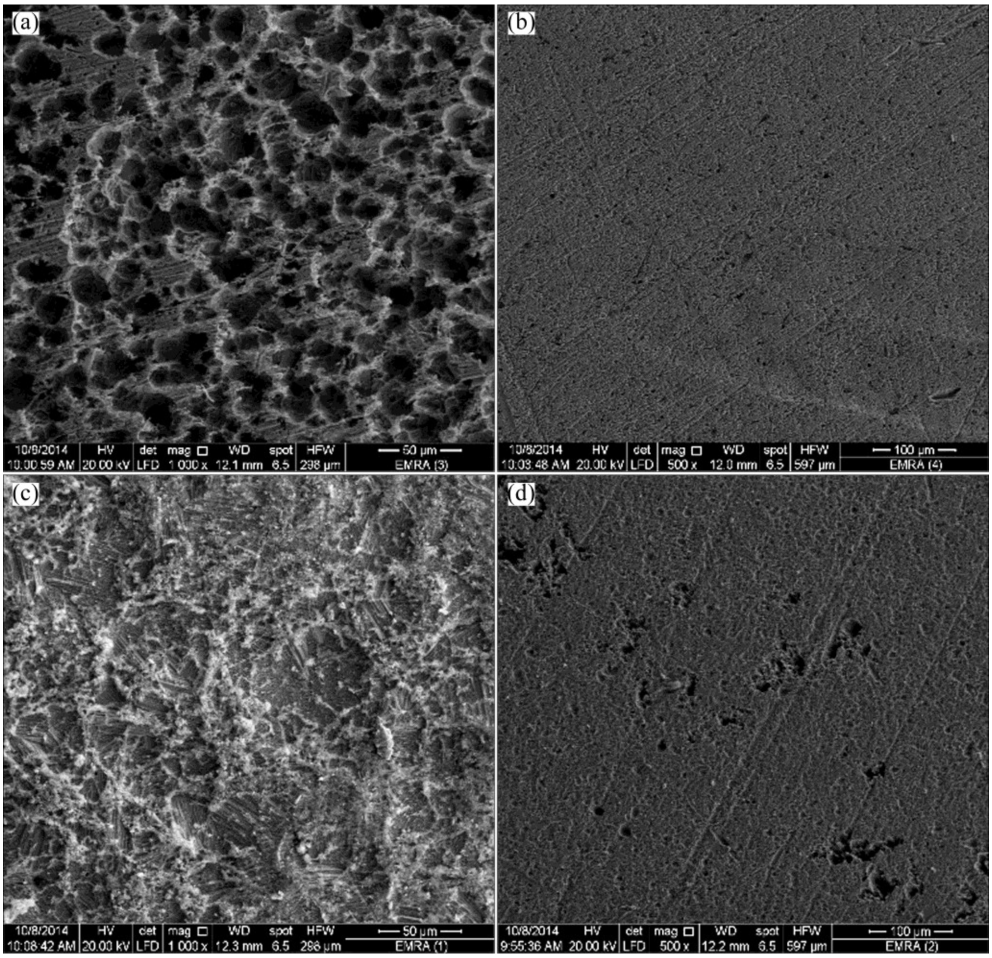

Fig. 1 SEM images of Zn immersed in 2.0 mol/L H_2SO_4 and 2.0 mol/L HCl solutions for 1 and 0.5 h, respectively in absence (a, c) and presence (b, d) of 200 mL/L fenugreek extract

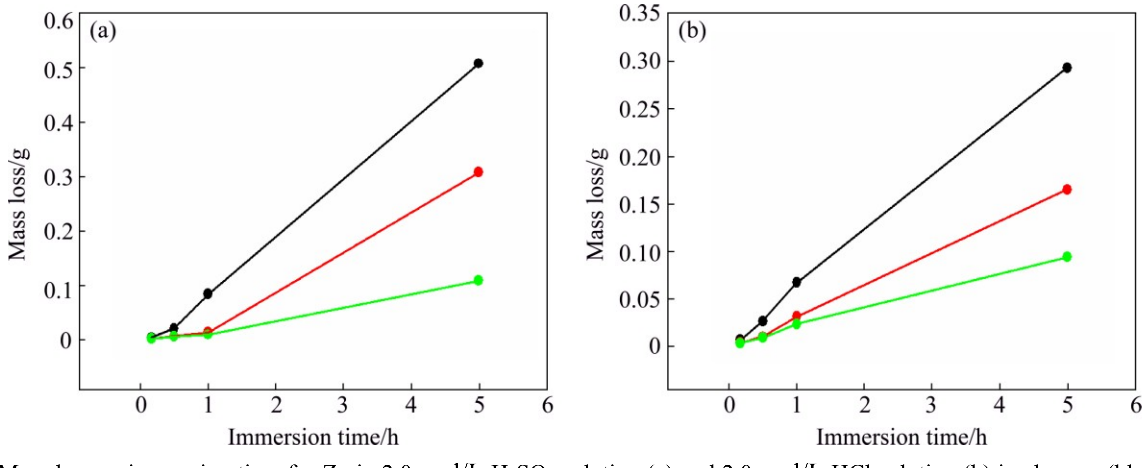

Fig. 2 Mass loss vs immersion time for Zn in 2.0 mol/L H_2SO_4 solution (a) and 2.0 mol/L HCl solution (b) in absence (black line) and presence of 50 mL/L (red line) and 100 mL/L (green line) fenugreek extract

Increasing rate is largely decreased as indicated by the decreased slopes of red lines in both cases compared to black lines (control). This indicates that the fenugreek extract is indeed a corrosion inhibitor for Zn in both acidic media. The maximum inhibition efficiencies observed in 100 mL/L of fenugreek extract in 2.0 mol/L H_2SO_4 and 2.0 mol/L HCl solutions are 86.7% after 1 h and 63.4% after 0.5 h, respectively.

3.3 Effect of fenugreek extract concentration and adsorption isotherm

The effect of various fenugreek extract concentrations on the corrosion behavior of Zn in 2.0 mol/L H_2SO_4 and 2.0 mol/L HCl solutions was studied by the mass loss method at immersion time of 1 h and 0.2 h, respectively and 28 °C. Figure 3 shows the variations of corrosion rate and inhibition efficiency of Zn in both acidic media with fenugreek extract concentration. It was found that by increasing the inhibitor concentration, the corrosion rate is decreased and the inhibition efficiency is increased. The inhibition ability of fenugreek is due to its adsorption on the metal surface, thus isolates the metal surface from the corrosive medium [12,13]. The maximum inhibition efficiencies of fenugreek extract (200 mL/L for Zn corrosion) are 90.7% and 66.6% in H_2SO_4 and HCl solutions, respectively. This indicates that the fenugreek extract is a good inhibitor in H_2SO_4 solution, while in HCl solution, its inhibition ability is moderate. This ability is enhanced by adding KI electrolyte.

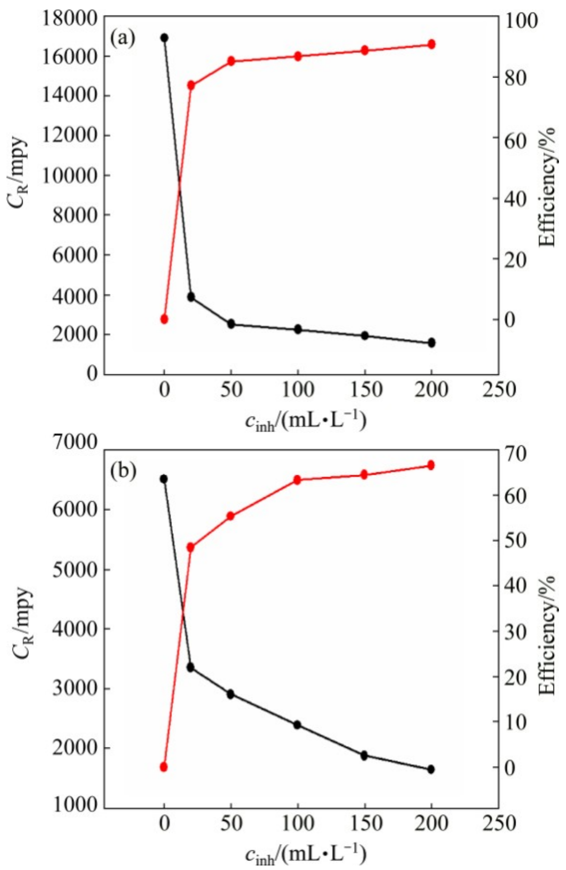

Fig. 3 Variations of corrosion rate (black line) and inhibition efficiency (red line) of Zn in 2.0 mol/L H_2SO_4 solution (a) and 2.0 mol/L HCl solution (b) with fenugreek concentration

From the mass loss data, the surface coverage (θ) values for different inhibitor concentrations in both acidic media have been evaluated. Then, Langmuir adsorption isotherm is applied to identifying the adsorption mechanism of fenugreek on Zn substrate. According to Langmuir isotherm:

$$\frac{c_{inh}}{\theta}=\frac{1}{K_{ads}}+c_{inh} \tag{4}$$

$$K_{ads}=\frac{1}{c_{H_2O}}\exp\left(\frac{\Delta G_{ads}}{RT}\right) \tag{5}$$

where c_{inh} is the inhibitor concentration (mL/L) in the electrolyte, K_{ads} (L/mL) is the equilibrium constant for the adsorption/desorption process, c_{H_2O} is the concentration of water molecules (mL/L) at the metal/solution interface, ΔG_{ads} is the standard free energy (J/mol), R is the universal gas constant (8.314 J/(mol·K) and T is the temperature in K.

Figure 4 shows the linear dependence of c_{inh}/θ against c_{inh}, an excellent fit is clearly presented by

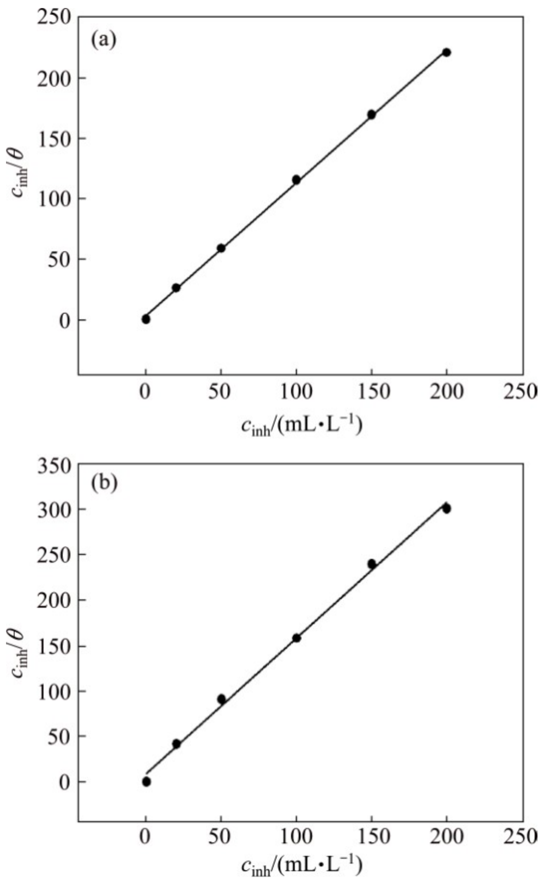

Fig. 4 Langmuir isotherms of Zn in 2.0 mol/L H_2SO_4 solution (a) and 2.0 mol/L HCl solution (b)

applying Langmuir isotherm for both acids. The correlation coefficient values, r^2, of fitted data are very close to 1 (0.9994 and 0.9967), the slope is almost unity, 1.0995, for H_2SO_4 medium, however, it deviates from unity, 1.4915 for HCl solution, reflecting the weak inhibitor adsorption on zinc surface in HCl medium as indicated by adsorption constant values of 0.3370 and 0.1122 for H_2SO_4 and HCl solutions, respectively [8,14]. This indicates that the adsorption of fenugreek extract on Zn surface in both media obeys the Langmuir adsorption isotherm, there is no interaction between the adsorbate molecules and they only occupy one site.

The value of standard free energy of adsorption (ΔG_{ads}) is determined using the equation:

$$\Delta G_{ads} = -2.303RT\lg(55.5K_{ads}) \tag{6}$$

Calculated ΔG_{ads} values for H_2SO_4 and HCl solutions are −7.33 and −4.58 kJ/mol, respectively. The negative values of ΔG_{ads} indicate spontaneous interaction of inhibitor species with the metal surface. Generally, if values of ΔG_{ads} are −20 kJ/mol or more, a physical mode of adsorption is suggested while, values of −40 kJ/mol or less indicate chemisorption [15]. So, it can be concluded that fenugreek extract adsorbed in both acidic media by an electrostatic interaction with charged Zn surface, however, the inhibitor has a better performance in H_2SO_4 solution than in HCl solution.

3.4 Temperature effect

Mass loss measurement was carried out at various temperatures (288 to 328 K) in the absence and presence of 100 mL/L fenugreek extract in both acidic media at immersion period of 1 h for 2.0 mol/L H_2SO_4 solution and 0.5 h for 2.0 mol/L HCl solution (Fig. 5). The corrosion rates of Zn in both acidic media increase with temperature rise both in uninhibited and inhibited solutions and it is more pronounced for uninhibited solution (control). On the other hand, the inhibition efficiency of fenugreek decreases with increasing temperature, as by increasing temperature, the corrosion rate and therefore the surface roughness is increased which leads to a decreased surface coverage of fenugreek on the metal. In other words, desorption of fenugreek rather than adsorption is favored, which suggests that the adsorption of fenugreek on Zn is physical adsorption.

Thermodynamics parameters, activation energy E_a, enthalpy and entropy changes ΔH and ΔS were calculated from Arrhenius and transition-state equations in absence and presence of inhibitor and listed in Table 1.

According to Arrhenius and transition-state equations:

$$\ln C_R = \ln A - \frac{E_a}{RT} \tag{7}$$

$$\ln\left(\frac{C_R}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S}{R} + \frac{\Delta H}{RT} \tag{8}$$

where C_R is the corrosion rate, A is the Arrhenius pre-exponential factor, h is Planck's constant, and N is Avogrado's number.

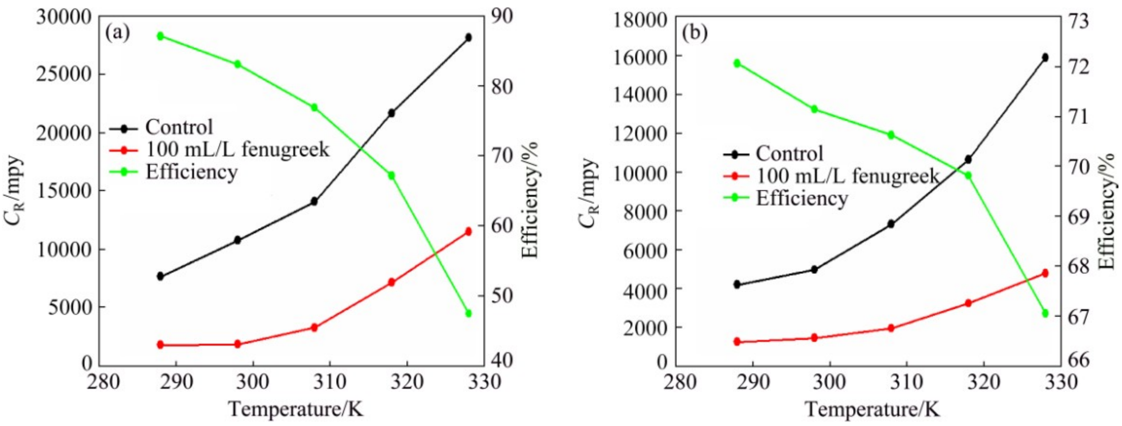

Fig. 5 Variations of corrosion rates and inhibition efficiency of Zn in 2.0 mol/L H_2SO_4 (a) and 2.0 mol/L HCl (b) in absence (control) and presence of 100 mL/L fenugreek extract at different temperatures

Table 1 Calculated values of activation energy (E_a), enthalpy change (ΔH) and entropy change (ΔS) of adsorption in absence and presence of 100 mL/L of fenugreek extract

Solution	Control				Fenugreek			
	ΔS/ (J·mol^{-1}·K^{-1})	ΔH/ (kJ·mol^{-1})	E_a/ (kJ·mol^{-1})	(E_a−ΔH)/ (kJ·mol^{-1})	ΔS/ (J·mol^{-1}·K^{-1})	ΔH/ (kJ·mol^{-1})	E_a/ (kJ·mol^{-1})	(E_a−ΔH)/ (kJ·mol^{-1})
H_2SO_4	−101.92	19.56	22.11	2.55	−54.61	37.41	39.96	2.55
HCl	−91.72	24.27	26.82	2.55	−100.18	24.83	27.38	2.55
KI/HCl	−74.04	29.45	32.00	2.55	−44.57	41.47	44.02	2.55

Figures 6 and 7 show potentiodynamic plots between ln C_R and ln(C_R/T) vs 1/T for corrosion of Zn in 2.0 mol/L H_2SO_4 (a) and 2.0 mol/L HCl (b) solutions in the absence and the presence of 100 mL/L of fenugreek, respectively. It can be concluded from Table 1 that the presence of fenugreek in 2.0 mol/L H_2SO_4 solution enhances E_a as a result of the increased energy barrier of the corrosion reaction in the inhibited solution as adsorbed fenugreek layer on the Zn retards its corrosion rate [16,17]. On the other hand, E_a is almost unchanged by adding fenugreek in 2.0 mol/L HCl solution, suggesting that fenugreek extract alone is not an efficient inhibitor for Zn corrosion in HCl medium.

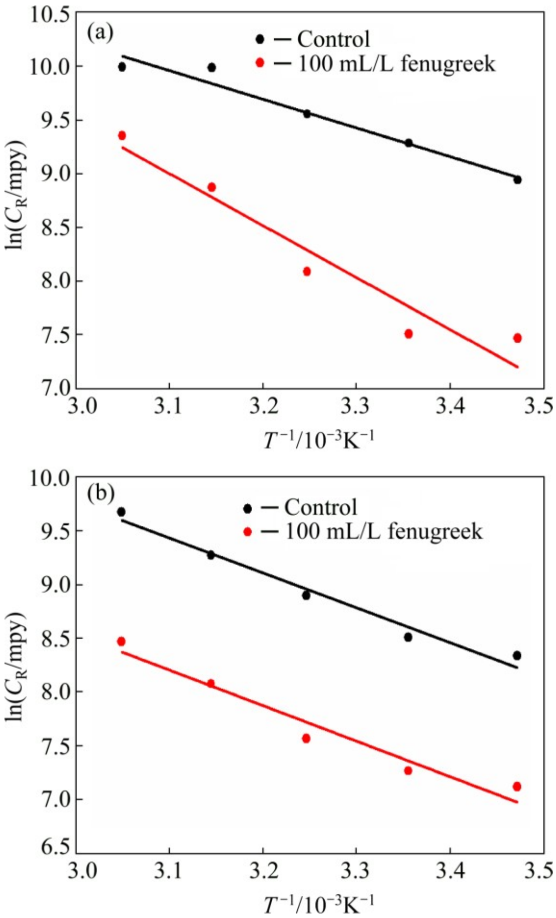

Fig. 6 Arrhenius plots of Zn in 2.0 mol/L H_2SO_4 (a) and 2.0 mol/L HCl (b) solutions

The ΔH value is higher in inhibited solution than that in uninhibited one, in the case of H_2SO_4 solution, suggesting that the Zn dissolution is slower in the presence of the fenugreek extract. The positive signs of ΔH means that Zn dissolution is an endothermic process. While, in the case of HCl solution, ΔH value is again almost unchanged. This agrees well with calculated E_a values in both acidic media. It can be shown in Eq. (9) that the difference between E_a and ΔH values equals RT, as shown in Table 1, especially in the case of H_2SO_4 solution.

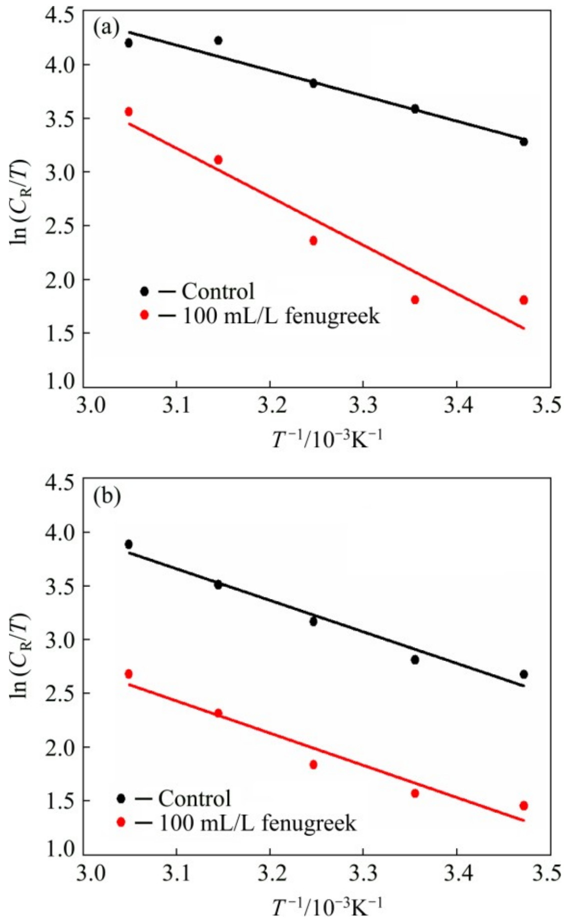

Fig. 7 Transition-state plots of Zn in 2.0 mol/L H_2SO_4 solution (a) and 2.0 mol/L HCl solution (b)

$$\Delta H=E_a-RT \tag{9}$$

The large and negative sign of ΔS in both inhibited and uninhibited solutions indicates that the activated complex in the rate-determining step is associative rather than dissociative [18,19]. Moreover, ΔS is less negative in inhibited solution containing fenugreek than that obtained in the uninhibited solution, H_2SO_4 solution. This behavior can be interpreted as a result of the replacement process of water molecules during adsorption of fenugreek on Zn surface [20,21]. Unchanged ΔS values in both inhibited and uninhibited HCl solutions reflect the weak adsorption ability of fenugreek on Zn surface, therefore, the weak inhibition ability of fenugreek for Zn corrosion in HCl solution.

3.5 Improving inhibition efficiency of fenugreek for Zn corrosion in HCl solution

To improve the inhibition ability of fenugreek seeds extract for Zn corrosion in HCl solution, an electrolyte, KI, is added in different concentrations to both uninhibited and inhibited HCl media. Inhibition efficiency values are calculated by the mass loss method and listed in Table 2.

Table 2 Inhibition efficiency values (η) of 10% fenugreek extract for Zn in 2.0 mol/L HCl as function of KI concentration

KI concentration/ $(mol \cdot L^{-1})$	η/% KI in 2.0 mol/L HCl	η/% KI+100 mL/L fenugreek in 2.0 mol/L HCl	S_θ
0.00	−	64.58	−
0.03	34.78	83.95	1.44
0.05	35.21	84.82	1.51
0.06	36.47	86.02	1.61

It can be shown that by increasing the KI concentration, the inhibition efficiency is increased in both cases. However, in the absence of the inhibitor, KI alone has a very low inhibition efficiency, but when being added to the acidic inhibitor solution, a synergistic effect between fenugreek extract and iodide anion is observed. The inhibition efficiency is 63.4% in the presence of only 100 mL/L fenugreek and 36.5% in the presence of only 0.06 mol/L KI. By combining both 0.06 mol/L KI and 100 mL/L fenugreek, the inhibition efficiency reaches 86.0%.

The synergistic effect was evaluated using parameter S [22,23]. The values of S can be calculated using the following equation and listed in Table 2:

$$S_\theta = \frac{(1-\Theta_{1+2})}{(1-\Theta'_{1+2})} \quad (10)$$

where $\Theta_{1+2}=\Theta_1+\Theta_2-\Theta_1\Theta_2$, Θ_1, Θ_2 and Θ'_{1+2} are surface coverage by I^- ion, by fenugreek and by combined I^- and fenugreek, respectively.

Moreover, the effect of the fenugreek extract concentration on the corrosion rate of Zn in (0.06 mol/L KI + 2.0 mol/L HCl) and 2.0 mol/L HCl solutions was investigated, as shown in Fig. 8. It is clear that the presence of I^- ion results in decreased corrosion rates at all fenugreek extract concentrations.

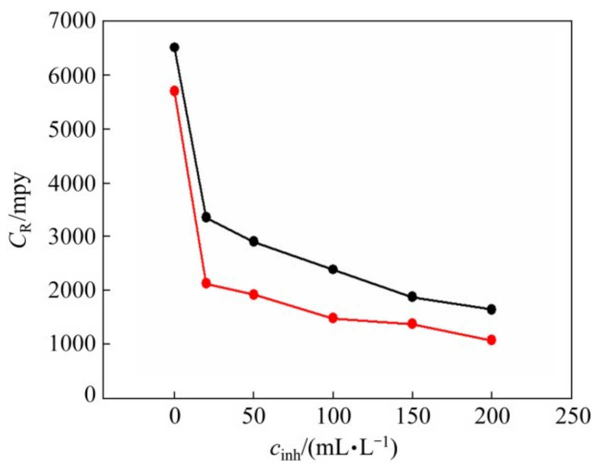

Fig. 8 Variation of corrosion rate with fenugreek extract concentration for Zn in 2.0 mol/L HCl in absence (black line) and presence (red line) of 0.06 mol/L KI

The variation of the corrosion rate of Zn in (0.06 mol/L KI + 2.0 mol/L HCl) solution with temperature in the absence and presence of 100 mL/L fenugreek extract was studied. The corrosion rate increases with temperature rise in both uninhibited and inhibited solutions and it is more pronounced for uninhibited solution. Thermodynamics parameters, activation energy E_a, enthalpy and entropy changes ΔH and ΔS were calculated from Arrhenius and transition-state equations in absence and presence of the inhibitor and listed in Table 1. The calculated activation energy values in the HCl solution containing iodide anion is higher than those calculated in HCl solution. This increase is more pronounced in the presence of the inhibitor, as shown in Table 1. These results support the existence of a synergism between fenugreek and iodide ions, which leads to an enhanced inhibition ability of fenugreek for Zn corrosion in HCl solution.

3.6 Inhibitor constituents and inhibition mechanism

The active constituents in fenugreek plant are alkaloids, amino acids, saponins, seroidal sapinogens, fiber, coumarin, lipids, vitamins and minerals [24]. As noticed, fenugreek plant contains a wide variety of N-containing compounds, such as amines which exist in aqueous acidic solutions in the form of onium ions. The metal surface is negatively charged due to the adsorption of negatively charged sulfate and chloride anions. Thus, electrostatic attraction between negatively charged metal surface and onium ions occurs, resulting in an adsorbed inhibitor film on the metal surface which inhibit metal ions to enter the solution (metal dissolution) [6]. Moreover, it was reported [25] that organic amine-type inhibitors can compete with the anions of the acid (sulfate and chloride ions) for position on the water-covered metal surface. Chloride ions, of smaller size and having no primary hydration sheaths, are more strongly adsorbed on the positively charged metal surface than the heavily hydrated ions of sulphate. Thus, fenugreek can be adsorbed on the metal surface, more strongly in H_2SO_4 solution than in HCl solution, which agrees well with the research results, in which the inhibition ability of fenugreek for Zn corrosion in H_2SO_4 solution is much better than that in HCl solution. The inhibition efficiency of fenugreek in HCl solution can be increased by adding iodide anions, as the moderately adsorbed iodide anions partially replace strongly adsorbed chloride anions on the metal surface, allowing a better chance for fenugreek adsorption compared to the case of HCl solution only.

3.7 XPS measurements

XPS analysis was done to identify the corrosion product of Zn in HCl medium and to prove and identify the nature of adsorption of fenugreek on Zn surface. XPS spectra for pure fenugreek (C 1s, O 1s and N 1s), Zn immersed in 2.0 mol/L HCl solution for 0.5 h (Zn $2p^3$, Cl 2p and O 1s) and Zn immersed in 200 mL/L of fenugreek extract in 2.0 mol/L HCl solution for 0.5 h (Zn $2p^3$, Cl 2p, C 1s, O 1s and N 1s) were obtained (Fig. 9). The N 1s XPS spectrum for pure fenugreek shows one peak located at 400 eV (Fig. 9(a_1)). This is corresponding to

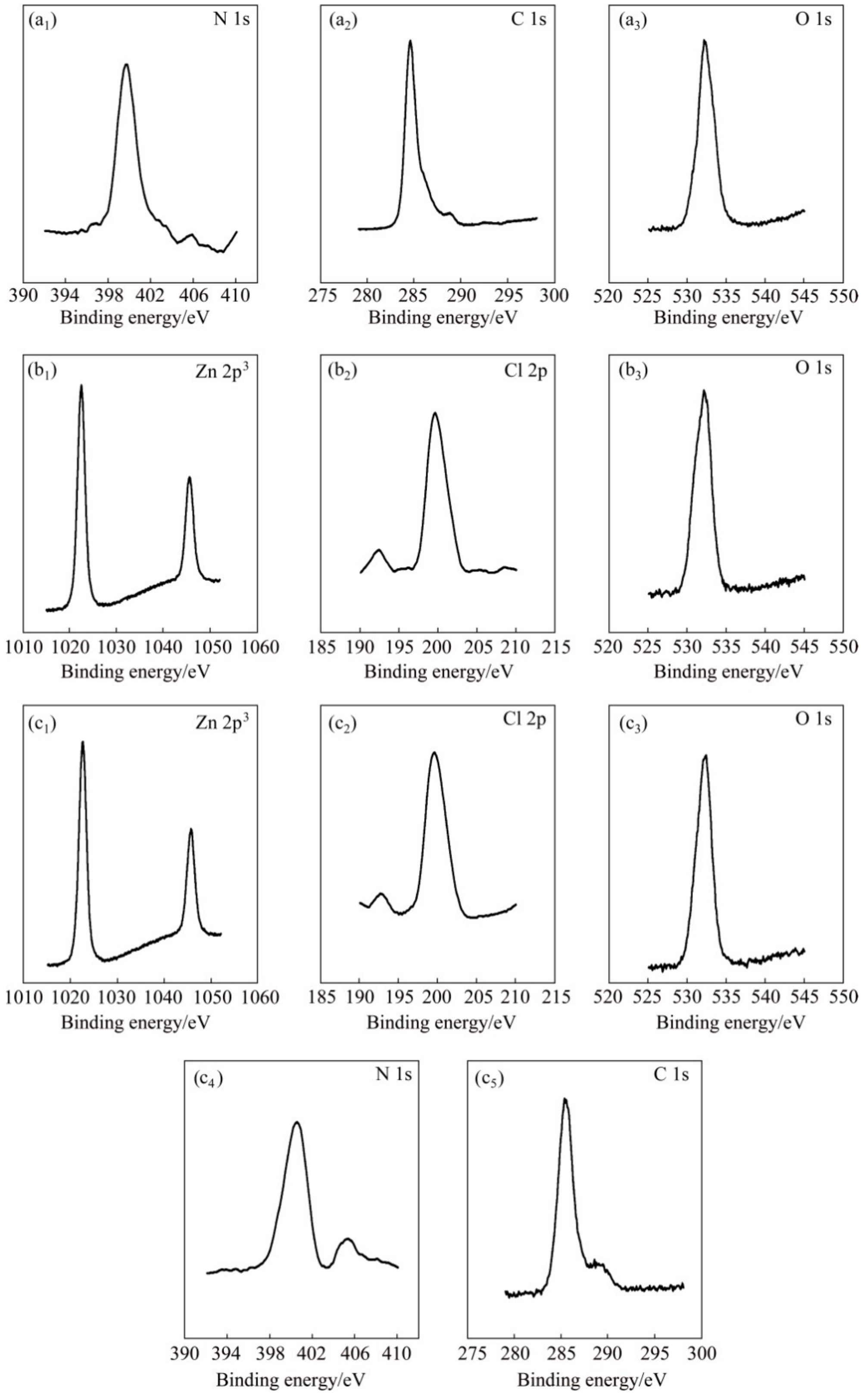

Fig. 9 XPS spectra for pure fenugreek (a_1−a_3) (C 1s, O 1s and N 1s) and Zn immersed in 2.0 mol/L HCl solution for 0.5 h (b_1−b_3) (Zn $2p^3$, Cl 2p and O 1s) and (c_1−c_5) Zn immersed in 200 mL/L of fenugreek extract in 2.0 mol/L HCl solution for 0.5 h (Zn $2p^3$, Cl 2p, C 1s, O 1s and N 1s)

amino groups [26]. C 1s spectrum shows two peaks, the main peak at 285 eV can be attributed to hydrocarbons [27] and the small peak at 289 eV is attributed to C—N bonds [28]. O 1s spectrum shows one peak at 533 eV, which is associated with the presence of oxygen in the adsorbed water [29]. The O 1s spectrum of Zn immersed in 2.0 mol/L HCl solution (Fig. 9(b_3)), shows one peak located at 531 eV, which is attributed to oxide anion, oxygen atoms bonded to Zn in Zn oxide (corrosion product) [30]. The N 1s spectrum of Zn immersed in acidic solution of fenugreek (inhibited solution) (Fig. 9(c_4)), shows one peak at 401 eV, which is attributed to the positively charged nitrogen of the protonated amino groups. It is known that the positive polarization of the nitrogen atom increases the binding energy [31]. The adsorption of fenugreek on the Zn surface can be proved by the appearance of nitrogen species in the XPS spectrum (Fig. 9(c)). Since the spectrum of Zn immersed in HCl solution (uninhibited solution) reveals the absence of N 1s analysis. This XPS result agrees well with the assumption that the fenugreek was electrostatically adsorbed on the Zn surface (physical rather than chemical mode of adsorption).

3.8 Electrochemical measurements

3.8.1 Potentiodynamic polarization

Figure 10 shows potentiodynamic polarization curves of Zn electrode in 2.0 mol/L HCl solution at 28 °C in the absence and presence of different concentrations of fenugreek extract.

Parameters obtained from the polarization curves are listed in Table 3. These include anodic (β_a) and cathodic (β_c) Tafel slopes, corrosion potential (φ_{corr}), and corrosion current density (J_{corr}) determined by extrapolation of the Tafel lines. Also, the inhibition efficiency η calculated according to Eq. (11):

$$\eta = \frac{J_{corr(0)} - J_{corr}}{J_{corr(0)}} \times 100\% \quad (11)$$

where $J_{corr(0)}$ and J_{corr} are the corrosion current densities in the absence and presence of fenugreek extract, respectively.

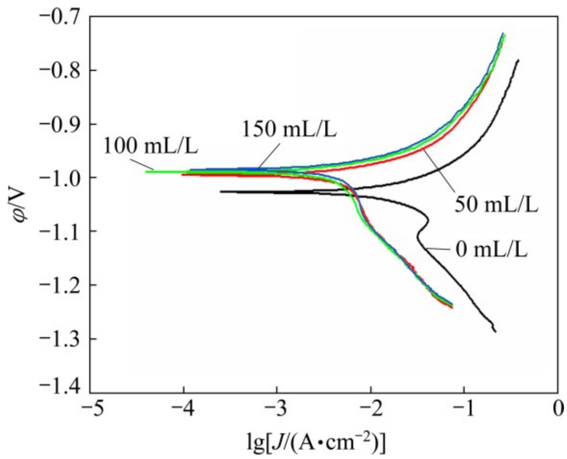

Fig. 10 Potentiodynamic polarization curves for Zn electrode in 2.0 mol/L HCl solutions in absence and presence of different fenugreek extract concentrations at 28 °C

The presence of fenugreek extract reduces the corrosion current density J_{corr} and the decrease in current increases as fenugreek extract concentration increases. The corrosion potentials (φ_{corr}) shift to more positive values in presence of the inhibitor, indicating that the inhibitor has a stronger effect on the anodic zinc dissolution than on the oxygen cathodic reduction. Thus, fenugreek can be considered as a mixed inhibitor that acts preferably on the anodic sites [32]. Anodic and cathodic Tafel slopes (β_a and β_c) do not change largely by the presence of the inhibitor, suggesting that the adsorption of fenugreek on Zn surface does not affect the corrosion mechanism. The inhibition efficiency η values increase by increasing the inhibitor concentration, and the obtained values agree well with those obtained by gravimetric measurements.

3.8.2 Electrochemical impedance spectroscopy (EIS)

The effect of fenugreek extract concentration on the impedance spectra, Bode and Nyquist plots, of Zn electrode in 2.0 mol/L HCl solution at 28 °C are shown in Fig. 11.

Nyquist plots consist of capacitive loops, thus Zn corrosion in uninhibited and inhibited HCl solutions is charge transfer controlled. The addition of the inhibitor

Table 3 Electrochemical parameters obtained from potentiodynamic polarization measurements and corresponding surface coverage and inhibition efficiency values for Zn in 2.0 mol/L HCl solutions in absence and presence of different fenugreek extract concentrations at 28 °C

Inhibitor concentration/ ($mL \cdot L^{-1}$)	J_{corr}/ ($mA \cdot cm^{-2}$)	φ_{corr}/ mV	β_c/ ($mV \cdot dec^{-1}$)	β_a/ ($mV \cdot dec^{-1}$)	θ	η/%
0	5.38	−1026.1	31.69	25.21	–	–
50	2.45	−994.32	35.18	20.51	0.55	54.46
100	2.01	−988.93	39.62	24.96	0.63	62.64
150	1.89	−984.42	35.86	20.59	0.65	64.83

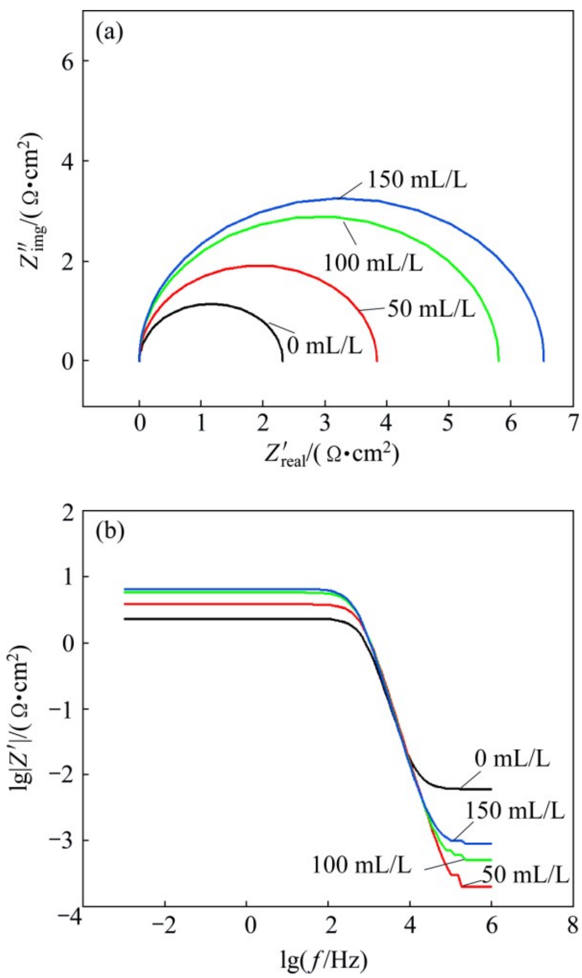

Fig. 11 Nyquist (a) and bode (b) plots for Zn electrode in 2.0 mol/L HCl solutions in absence and presence of different fenugreek extract concentrations at 28 °C

at any concentration does not change the shape of Nyquist plots, which means that the corrosion mechanism is not changed by the presence of the inhibitor as previously mentioned. Data were fitted by using the electrical equivalent circuit shown in Fig. 12. The equivalent circuit consists of a double layer capacitor (C_{dl}) in parallel with a charge-transfer resistance (R_{ct}).

Values of R_{ct} were calculated from the difference in impedance at low and high frequencies, the percent

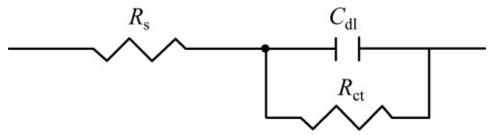

Fig. 12 Electrical equivalent circuit used for fitting impedance data for Zn electrode in 2.0 mol/L HCl at 28 °C

inhibition efficiency η was calculated according to Eq. (12) [32]:

$$\eta = \left[1 - \frac{R_{ct(0)}}{R_{ct}}\right] \times 100 \qquad (12)$$

where $R_{ct(0)}$ and R_{ct} are charge transfer resistances in the absence and presence of the inhibitor, respectively.

The impedance parameters obtained by fitting the Nyquist plots and the calculated inhibition efficiency are listed in Table 4.

Values of R_{ct} are larger in the presence of the inhibitor compared to the control solution and this increase is more pronounced with increasing the inhibitor concentration. R_{ct} is related inversely to the corrosion rate and this trend indicates the inhibition ability of fenugreek for Zn corrosion in HCl medium. While, C_{dl} values tend to decrease with increasing the inhibitor concentration. This can be attributed to decrease in dielectric constant and/or increase in the thickness of electric double layer, suggesting that the inhibitor molecules act by adsorption mechanism at metal/acid interface.

4 Conclusions

1) Fenugreek extract can be used as an excellent green corrosion inhibitor for Zn in H_2SO_4 solution with a maximum efficiency of 90.7% at an immersion time of 1 h and by using 200 mL/L of the extract, however, the inhibition ability in HCl solution is moderate (66.6%). This can be contributed to the strongly adsorbed chloride anions (compared to the weakly adsorbed heavily hydrated sulfate anions) which decreases the adsorption extent of the inhibitor on the metal surface.

2) The adsorption of fenugreek extract on Zn surface obeys Langmuir adsorption isotherm.

Table 4 Electrochemical parameters obtained from Nyquist plots and corresponding surface coverage and inhibition efficiency values for Zn in 2.0 mol/L HCl solutions in absence and presence of different fenugreek extract concentrations at 28 °C

Inhibitor concentration/(mL·L^{-1})	R_S/ (Ω·cm^2)	R_S error/%	C_{dll}/ (10^{-5} μF·cm^{-2})	C_{dll} error/%	R_{CT}/ (Ω·cm^2)	R_{CT} error/%	θ	η/%
0	1.42	4.05×10^{-13}	9.49	1.21×10^{-13}	2.2	5.76×10^{-15}	–	–
50	0.74	9.50×10^{-12}	6.31	2.02×10^{-14}	3.95	7.01×10^{-16}	0.44	44.30
100	0.68	2.97×10^{-13}	5.45	3.87×10^{-17}	5.92	1.91×10^{-15}	0.63	62.84
150	0.70	9.19×10^{-14}	5.31	1.59×10^{-14}	6.35	9.66×10^{-15}	0.65	65.35

3) The calculated thermodynamics parameters suggest that fenugreek extract is a good inhibitor for Zn corrosion in H_2SO_4 solution, while, fenugreek alone is not an efficient inhibitor in HCl medium.

4) Combination of fenugreek extract with KI improves its inhibition efficiency for Zn corrosion in HCl by synergistic effect.

5) The decreased corrosion current and increased charge transfer resistance measured by potentiodynamic polarization and EIS measurements, respectively, reflect the inhibition ability of fenugreek for Zn corrosion in HCl solution.

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锌在酸性介质中的腐蚀控制：葫芦巴绿色抑制剂

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摘　要：利用葫芦巴种子提取物作为绿色腐蚀抑制剂，采用失重法和电化学方法研究锌在 2.0 mol/L 硫酸和 2.0 mol/L 盐酸中的腐蚀行为。扫描电子显微镜结果表明添加抑制剂后，锌的表面腐蚀得到减缓。光电子能谱分析表明腐蚀产物为 ZnO，验证了抑制剂的吸收机理。当添加 200 mL/L 葫芦巴提取物时，在硫酸溶液中腐蚀 1 h 和盐酸溶液中腐蚀 0.5 h 可得到最大抑制率，分别为 90.7%和 66.6%。在 HCl 溶液中添加 I^-离子时，由于协同作用可大幅度提高葫芦巴种子提取物对锌腐蚀的抑制率。动电位极化和 EIS 分析表明葫芦巴种子提取物对锌在盐酸中的腐蚀有抑制作用。添加葫芦巴种子提取物可降低腐蚀电流，增加电荷转移电阻。

关键词：锌；腐蚀机理；抑制剂；协同作用

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