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The Inhibitive Performance of *Fenugreek* for Corrosion of Copper and Nickel in Sulfuric Acid

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Fenugreek extract was examined as a corrosion inhibitor for copper and nickel in 2.0 M H_2SO_4 solution by gravimetric and electrochemical measurements. Scanning electron micrographs showed that the surface damage is decreased in inhibited acidic solution for both metals. The maximum inhibition efficiencies were 85.6% and 83.5% for copper and nickel, respectively, by using 20% (V/V%) of fenugreek extract in H_2SO_4 solution. Adsorption of fenugreek on both metals follows Langmuir adsorption isotherm. Florry-Huggins isotherm can be applied successively only in case of nickel suggesting a chemisorptions mode at later stages of adsorption process. Linear polarization and impedance measurements prove the inhibition ability of fenugreek for copper and nickel corrosion in H_2SO_4 solution.

Keywords: Natural Inhibitor; Corrosion; Thermodynamics, Polarization; Impedance.

1. INTRODUCTION

The problem of metals corrosion threaten many industries. Various prevention methods have been applied such as coating and alloying. The addition of substances that are capable of inhibiting corrosion rates is also well known [1, 2]. New scientific trends focus on the use of natural compounds or wastes as corrosion inhibitors, which are available, cheap, green and have most of times a considerable inhibition efficiency [3]. A famous category of naturally occurring corrosion inhibitors are plant extracts [4]. The reason of their inhibition ability is mainly due to the presence of hetero-atoms such as sulfur or oxygen which can bind physically or chemically to the metal surface thus, reduce its dissolution rate [5].

Several plant extracts were employed as green corrosion inhibitors for mainly aluminum and steel. For other metals such as copper and nickel, research papers are limited for examples, the corrosion of copper in various acidic media was reduced by cannabis plant [2], and tryptophan [6] in H_2SO_4 Egyptian licorice [7], chitosan [8], and jatropha curcas leaves [9] in HCl, Gnetum africana and musa acuminate peel [10] in HNO_3. The inhibition effect was also studied in alkaline NaOH medium, inula viscosa [11], and natural sea water, Mimusops elengi leaves [12], emblica officinalis [13], and caffeine [14]. While fewer plant extracts were previously reported for nickel such as extract of cannabis plant [15] and alanine [16] in H_2SO_4. The inhibition efficiency values of these plant extracts for copper corrosion in H_2SO_4 were 84.4 % [2] and 80.0 % [6]. Lower values were reported for nickel corrosion in H_2SO_4 solution, 73.0 % [15] and 65.23 % [16].

The inhibition efficiency has been increased by increasing the extract concentration [2-7,10,15,16] but decreased with temperature rise [6,10,16]. The inhibitor adsorption on copper or nickel surface obeys with Langmuir [2,8,10] or Temkin [7] adsorption isotherms. The Gibbs free energy of adsorption are less than 20 kJ/mol thus, the adsorption is physisorption [6]. Linear polarization curves showed that the plant extract can behave as anodic, cathodic [2] or mixed-type inhibitor [2,7,8].

In the present work, the inhibition ability of fenugreek extract for copper and nickel corrosion in 2.0 M H_2SO_4 solutions will be tested by gravimetric and electrochemical measurements such as linear polarization and electrochemical impedance spectroscopy (EIS). Several factors will be studied such as immersion time, inhibitor concentration and temperature, to identify best conditions for the inhibition performance of fenugreek. The proper adsorption isotherm will also be identified and important thermodynamics parameters will be calculated.

2. MATERIALS AND METHODS

2.1. Materials

Two metallic alloys will be tested:

- A copper sheet of the following composition (wt %): 0.4788 C, 0.6045 O, 0.1903 Al, and 98.7264 Cu.
- A nickel cylinder of the following composition (wt %): 1.1880 C, 1.0046 Mn, 0.5343 Si, 1.0813 O, 1.9038 Fe, 31.4343 Cu and 62.8537 Ni.

Pre-treatment of metallic 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, and then drying at room temperature before use.

The corrosive solution (2.0 M H_2SO_4) was prepared by dilution of H_2SO_4 (95-97% Sigma Aldrich) with purified water.

2.2. Preparation of fenugreek extract

Commercial seeds of fenugreek were obtained (~ 1 kg), grounded and boiled in distilled water for 1h. The extract was stand overnight, then filtered. Finally the filtrate was completed to 250 mL with purified water [17].

2.3. Gravimetric measurements

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

From the weight loss, the corrosion rates (R), surface coverage (θ) and inhibition efficiency percent (η%) can be calculated [17].

2.4 Electrochemical measurements

Electrochemical measurements were carried out using a Solartron SI 1287 and Frequency Response analyzer 1252A system. in a three electrode-one compartment cell with copper or nickel as the working electrode (exposed surface areas were 3.7 cm^2 for copper and 2.9 cm^2 for nickel), 3.0 M Ag/AgCl as a reference electrode, and a platinum coil as an auxiliary electrode. Linear polarization was carried out by scanning the potential at open-circuit corrosion potential (OCP)±0.25 V, scan rate = 1 mV s^{-1}. EIS was measured at OCP in the frequency range100 kHz to 0.1 Hz with 5 mV amplitude. Before polarization and EIS experiments, the OCP of the working electrode was measured with time till reached a constant value, time needed is ~ 5 min.

2.5. Surface characterization

The surface morphology was investigated by a scanning electron microscope (JCM 6000) with accelerating voltage of 15 kV.

3. RESULTS AND DISCUSSION

3.1. Surface characterization

Copper and nickel specimens were pre-treated as previously described, and then immersed in a 2.0 M H_2SO_4 solution with and without fenugreek seeds extract (20%, V/V%) at 25°C for 24 and 48 h, respectively. Surface deterioration can be observed upon immersing copper and nickel specimens in 2.0 M H_2SO_4, Fig.1: A and C, respectively. While, with the inhibitor in acidic solution, the extent of damage on the copper and nickel surface is largely decreased, Fig.1: B and D, respectively which indicates the inhibition action of fenugreek for copper and nickel in H_2SO_4 medium.

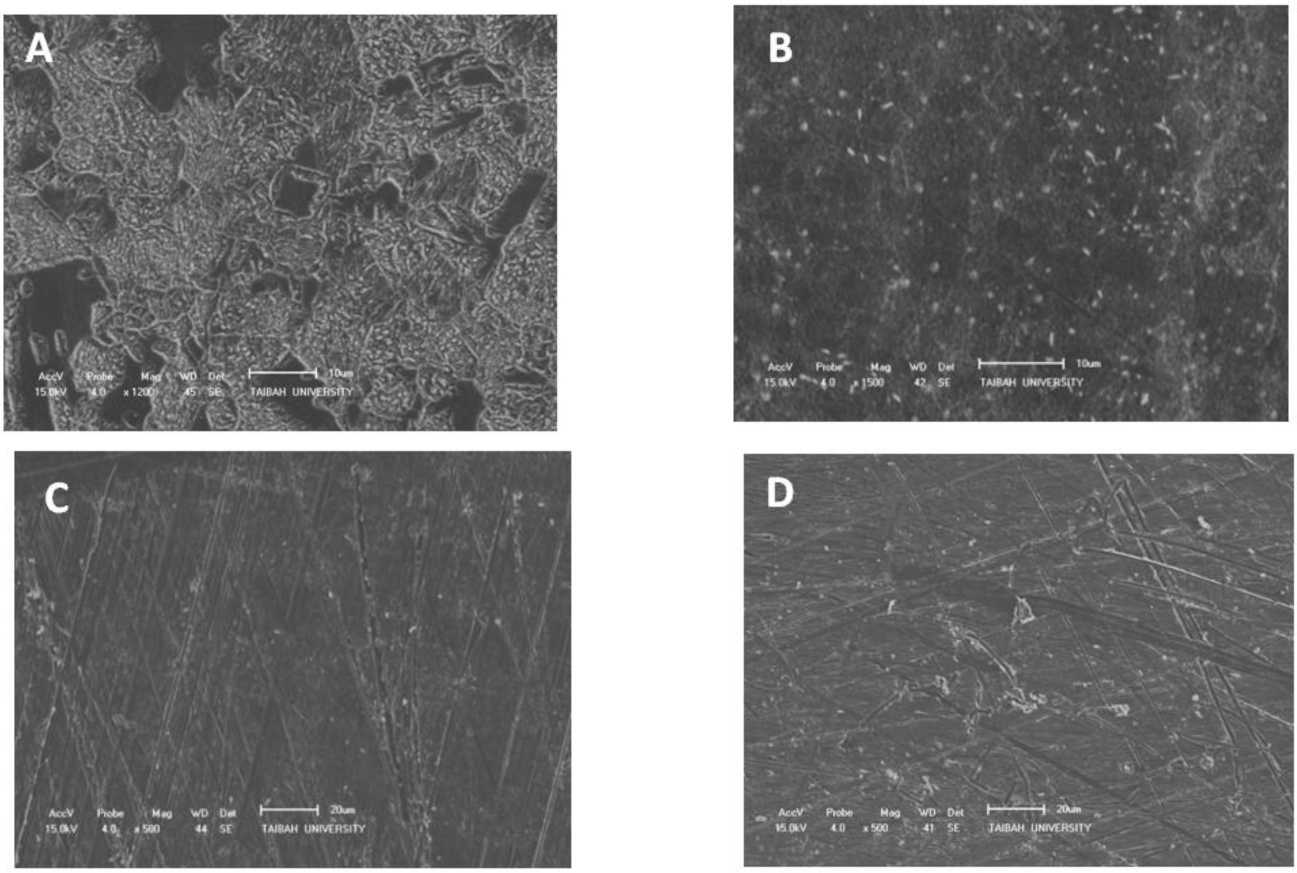

Figure 1. SEM images of copper and nickel immersed in 2.0 M H_2SO_4 for 24 and 48 h, respectively in the absence (A,C) and presence (B,D) of fenugreek extract.

3.2. Weight loss experiment: immersion time effect

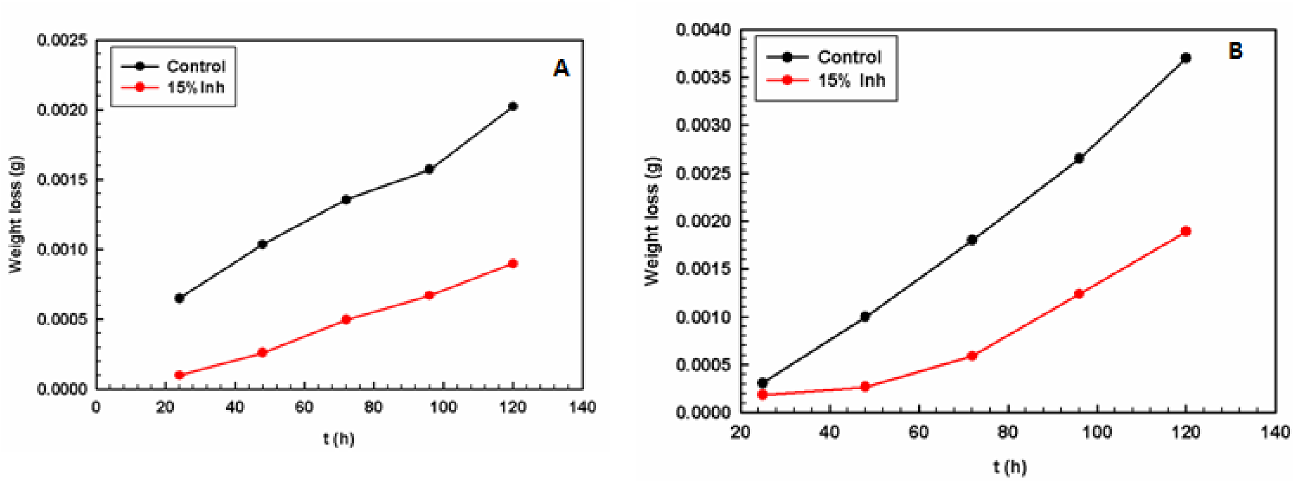

Figure 2. Weight loss vs. immersion time for (A) copper and (B) nickel in 2.0 M H_2SO_4 in the absence (back line) and presence of 15%, V/V% fenugreek extract (red line).

The change of weight loss of copper and nickel specimens in 2.0 M H_2SO_4 solutions, with and without (15%,V/V%) fenugreek seeds extract at 25 °C with an exposure time up to 120 h, is given in

Fig.2. It is clearly that the weight loss increased with increasing exposure time. However, this increase is much less by the addition of the extract. This indicates that fenugreek extract is a good corrosion inhibitor for the two metals in H_2SO_4 medium. The maximum inhibition efficiency values observed in 2.0 M H_2SO_4 solution for copper and nickel are 84.6 % after 24 h and 80.5 % after 48 h, respectively.

3.3. Effect of fenugreek extract concentration

The effect of the various extract concentrations on the corrosion behavior of both metals, copper and nickel, in 2.0 M H_2SO_4 was studied by the weight loss method at 25°C and an exposure time of 24 h and 48 h, respectively, as shown by Fig.3. The corrosion rate decreases while, the inhibition efficiency increases with increasing the inhibitor concentration. The corrosion parameters such as corrosion rate (R), surface coverage (θ) and inhibition efficiency percent (η%) and at different concentrations of fenugreek extract in 2.0 M H_2SO_4 at 25°C are presented in Table1.

Table 1. Corrosion rate, surface coverage and inhibition efficiency values for copper and nickel in absence and presence of different fenugreek extract concentrations in 2.0 M H_2SO_4 at 25°C.

[Inhibitor] (mL/L)	Copper			Nickel		
	R(mpy)	θ	***η*** %	R(mpy)	θ	***η***%
0	10.48	-	-	4.23	-	-
20	2.47	0.76	76.41	1.92	0.55	54.61
50	1.77	0.83	83.08	1.41	0.61	60.77
100	1.61	0.84	84.10	0.99	0.77	76.56
150	1.67	0.85	84.62	0.83	0.81	80.49
200	1.50	0.86	85.64	0.70	0.84	83.47

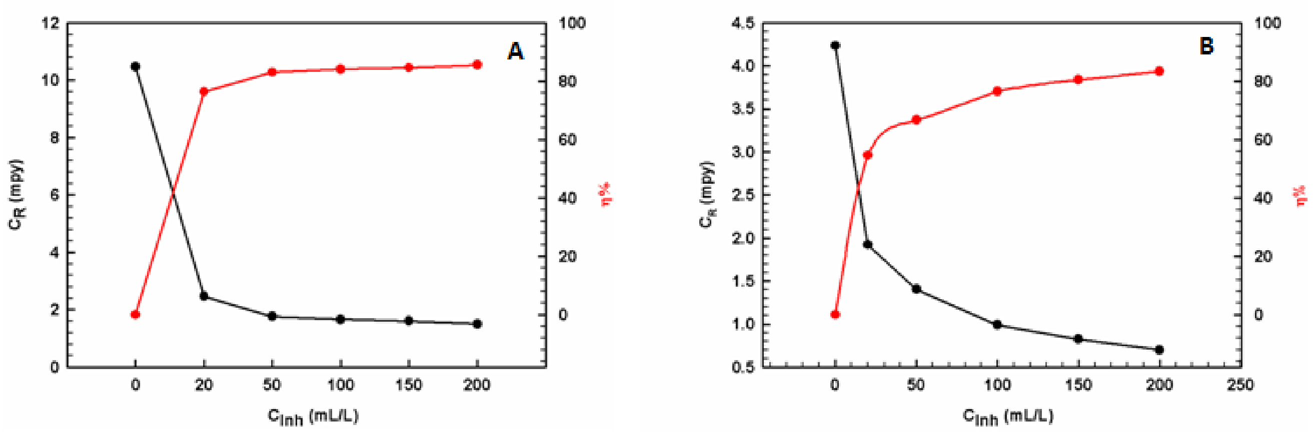

Figure 3. Variations of corrosion rate (black line) and inhibition efficiency (red line) of (A) copper and (B) nickel in 2.0 M H_2SO_4 with fenugreek concentration.

The corrosion inhibition efficiency of fenugreek extract (20%,V/V%) reaches 85.6% and 83.5% for copper and nickel in 2.0 M H_2SO_4 solution, respectively. This means that fenugreek extract has the highest inhibition ability for both metals corrosion, especially for nickel, compared to other green inhibitors reported in literature where, the highest inhibition efficiency values reported for copper and nickel corrosion in H_2SO_4 solutions were.84.4 [6] and 73.0 % [15], respectively.

Langmuir adsorption isotherm [15] was applied to investigate the adsorption mechanism of fenugreek extract on copper and nickel surfaces.

Fig.4 shows the linear dependence of C_{inh}/θ against C_{inh}. For both metals, an excellent fit is clearly presented, the linear correlation coefficient values, r^2, is 0.9997 and 0.9993 for copper and nickel, respectively. Thus, the adsorption of fenugreek extract on both metal surfaces in H_2SO_4 solution obeys Langmuir adsorption isotherm. Adsorption parameters obtained from Langmuir adsorption isotherm are estimated and listed in Table 2.

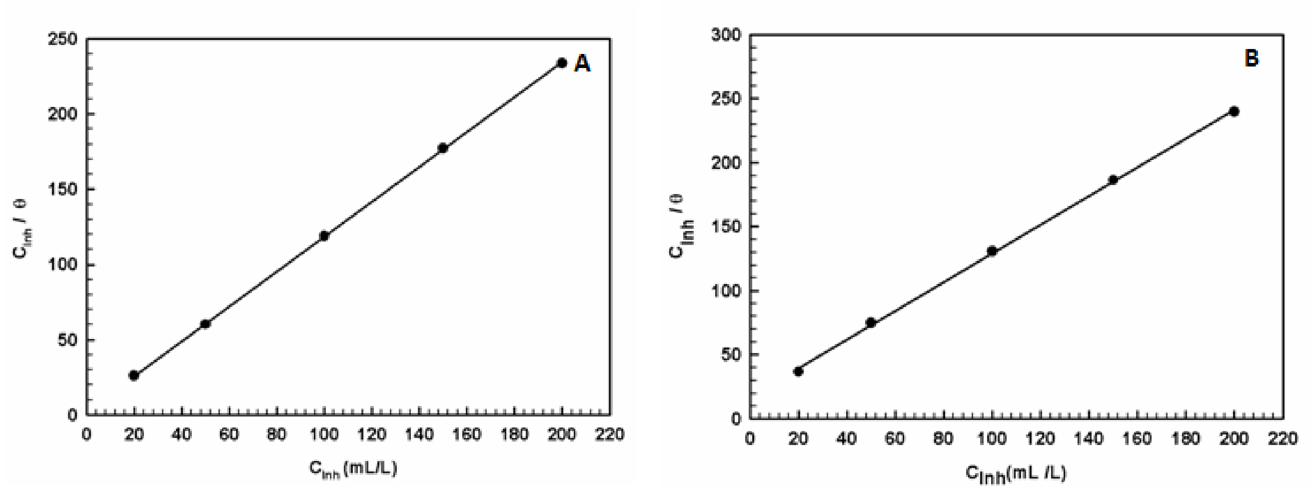

Figure 4. Langmuir isotherms of (A) copper and (B) nickel in 2.0 M H_2SO_4.

Table 2. Adsorption parameters of fenugreek extract in 2.0 M H_2SO_4 on copper and nickel surfaces from Langmuir and Florry-Huggins adsorption isotherms.

Copper				
isotherm	Slope	K_{ads} (L/mL)	r^2	ΔG_{ads} (kJ/mol)
Langmuir	1.16	0.3587	0.9999	-7.25
Nickel				
Langmuir	1.12	0.0590	0.9993	-2.26
Flory-Huggins	0.85	3.2755	0.9949	-12.94

Flory–Huggins isotherm was applied successfully in adsorption of several natural and organic compounds on steel [18-24] aluminum [25, 26] and nickel surface [15].

Fig.5 shows that Flory–Huggins isotherm can be applied for fenugreek adsorption on nickel (r^2= 0.9966) rather than copper (r^2= 0.8615) surface in H_2SO_4 medium. Therefore, it can be suggested that, for nickel only, the initial stage of inhibition mechanism involves physical adsorption at the metal/solution interface. Then, the electron pairs of nitrogens of the amino groups of fenugreek form coordination bonds with nickel atoms, i.e. chemisorptions occurs [27]. This assumption will be further ascertained by the activation energy value where, the activation energy for chemical adsorption is higher than 80 kJ/mol [28-30]. The value of x was approximately 1, which means that one fenugreek molecule is adsorbed on one active site, replacing one water molecule.

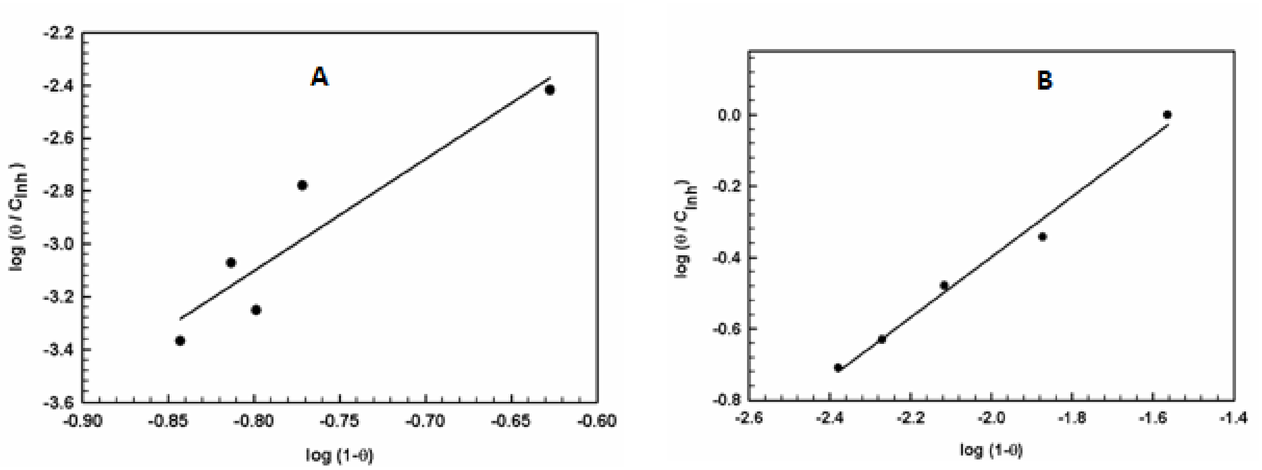

Figure 5. Florry-Huggins isotherms of (A) copper and (B) nickel in 2.0 M H_2SO_4.

The value of the standard free energy of adsorption (ΔG_{ads}) is determined using Equation (1) and found to be –7.25 and -12.94 kJ/mol K for copper and nickel, respectively.

$$\Delta G_{ads} = -2.303RT\log(55.5K_{ads}) \qquad (1)$$

The adsorption is spontaneous as values of ΔG_{ads} are negative. Generally, values of ΔG_{ads} around -20 kJ/mol or more are attributed to physical adsorption (electrostatic interactions between charged metal surface and the inhibitor) while values around -40 kJ/mol or less are due to chemisorption (coordinate bond) [15]. So, it can be concluded that fenugreek extract adsorbed by electrostatic interactions.

3.4. Temperature effect

Gravimetric measurement was carried out at various temperatures (288 to 328 K) with and without 15% (V/V%) fenugreek extract in 2.0 M H_2SO_4 at immersion period of 24 and 48 h for copper and nickel, respectively. Fig.6 shows the variations of the corrosion rates and inhibition efficiencies for both metals with temperature.

It can be seen that the corrosion rates of both metals in 2.0 M H_2SO_4 increase with temperature in both control and acidic inhibitor solution however, it is more pronounced for control solution. The inhibition efficiency of fenugreek decreases with increasing temperature, due to a decrease in the surface coverage. Thus, increased desorption i.e, a physical adsorption mode, this agrees with the calculated values of ΔG_{ads}.

Thermodynamics parameters, activation energy E_a, enthalpy ΔH and entropy ΔS changes were evaluated from the Arrhenius and Transition-state equations [17] with and without the inhibitor and listed in Table 3.

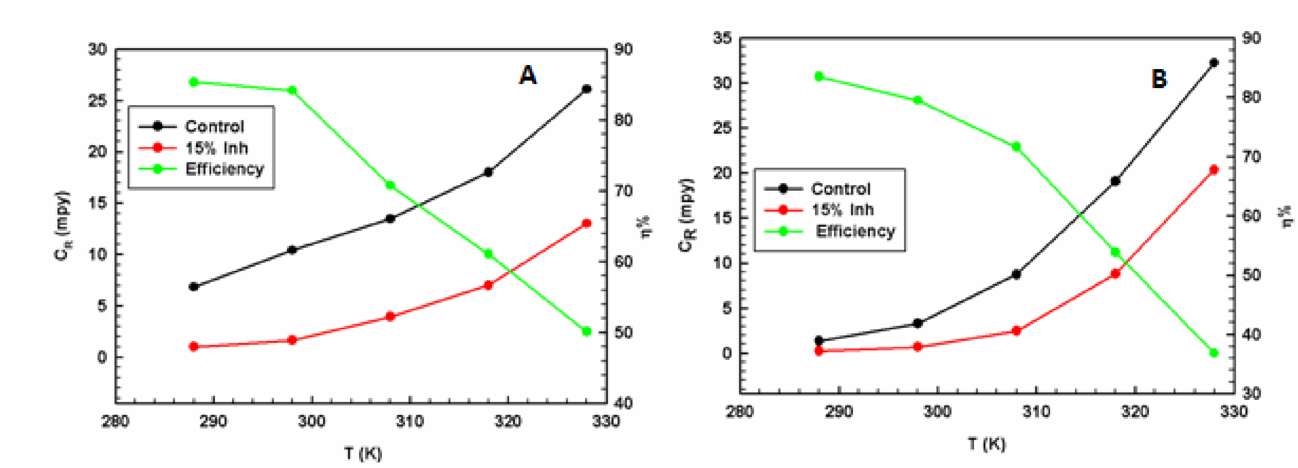

Figure 6. Variations of corrosion rates and inhibition efficiency of (A) copper and (B) nickel in 2.0 M H_2SO_4 in the absence (control) and presence of 15%, V/V% fenugreek extract at different temperatures.

Table 3. Calculated values of activation energy (E_a), enthalpy (*ΔH*) and entropy *(ΔS)* of adsorption in the absence and presence of 15%, V/V% of the fenugreek extract on copper and nickel surfaces.

Thermodynamics Parameters	Control				Fenugreek			
	Δ*S* (J/mol K)	**Δ*H* (kJ/mol)**	**E_a (kJ/mol)**	**E_a-Δ*H* (kJ/mol)**	**Δ*S* (J/mol K)**	**Δ*H* (kJ/mol)**	**E_a (kJ/mol)**	**E_a-Δ*H* (kJ/mol)**
Copper	**-149.36**	**22.79**	**25.35**	**2.55**	**-75.04**	**49.03**	**51.58**	2.55
Nickel	**-29.32**	**61.19**	**63.74**	**2.55**	**49.72**	**88.48**	**91.03**	2.55

Figs. 7 and 8 show linear plots between $\ln C_R$ and $\ln(C_R/T)$ vs 1/T for corrosion of copper and nickel in 2.0 M H_2SO_4 solutions in the absence and the presence of 15% (V/V%) of fenugreek extract.

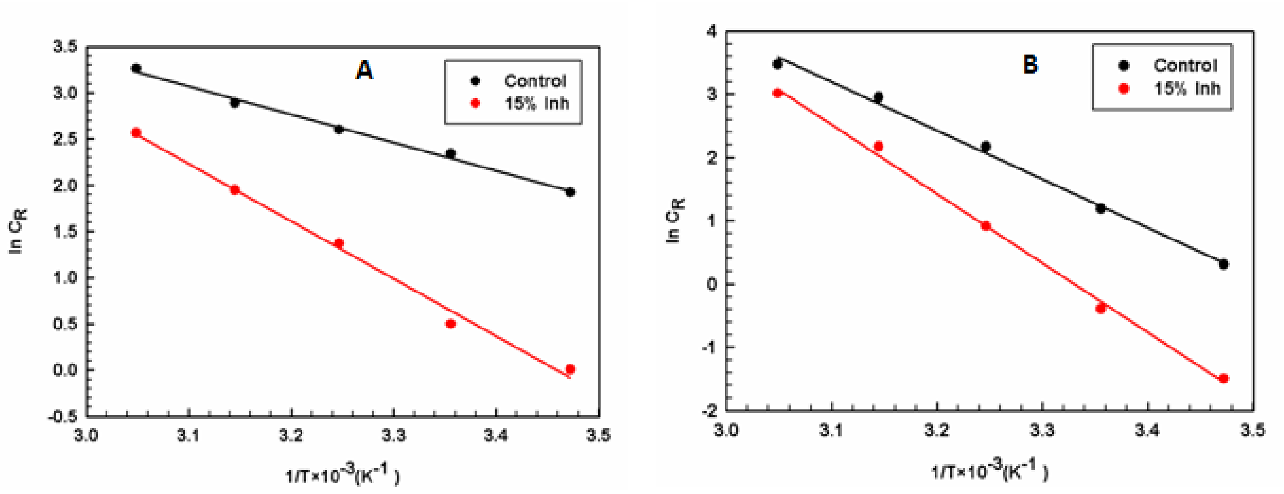

Figure 7. Arrhenius plots of (A) copper and (B) nickel in 2.0 M H_2SO_4.

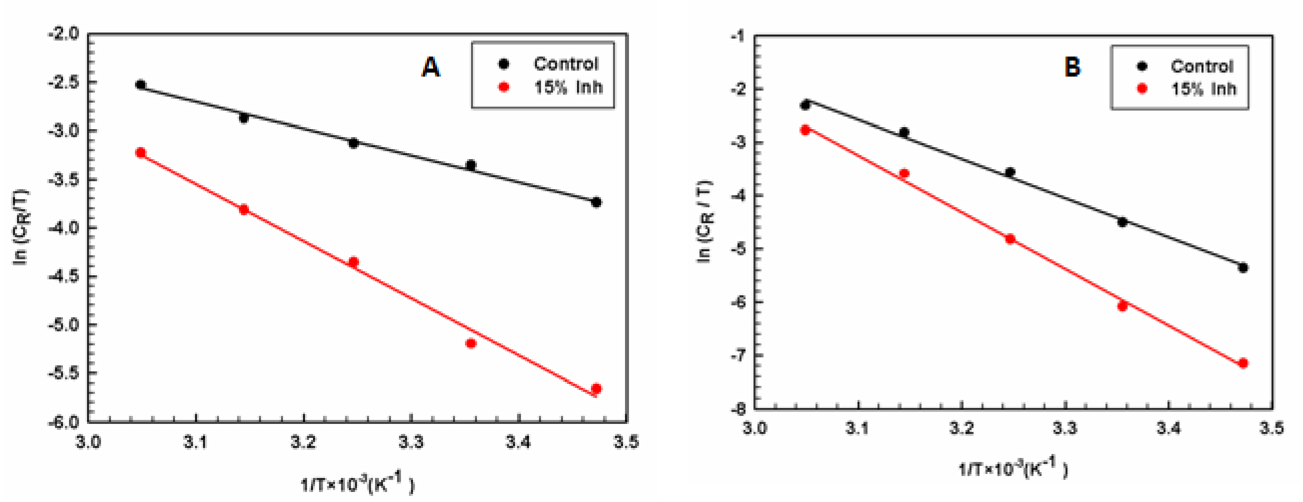

Figure 8. Transition-state plots of (A) copper and (B) nickel in 2.0 M H_2SO_4.

It can be concluded that, from Table 3, the presence of fenugreek in 2.0 M H_2SO_4 solution enhances E_a. In other words, the corrosion, metal dissolution, is retarded in the acidic inhibitor solution due to the protective adsorbed layer of fenugreek on metal surface [16, 17].

The positive signs of ΔH means that the metal dissolution is endothermic. The ΔH value is more positive in inhibited solution than that in H_2SO_4 solution, suggesting that the copper and nickel dissolution is slower in the presence of fenugreek extract. It can be shown that the difference between E_a and ΔH values is equal to RT, according to Equation (2):

$$\Delta H = E_a - RT \qquad (2)$$

The negative sign of ΔS indicates that the activated complex is associative rather than dissociative [31, 32]. Moreover, ΔS is less negative in inhibited solution containing fenugreek than that obtained in the uninhibited solution, in case of copper because of the replacement of water molecules upon fenugreek adsorption on copper surface [33, 34]. In case of nickel, the ΔS is more negative in the presence of the inhibitor as more water molecules can be desorbed from the metal surface by one inhibitor molecule [35].

3.5. Electrochemical measurements

3.5.1. Linear polarization

Fig.9 shows linear polarization curves of (A) copper and (B) nickel electrodes in 2.0 M H_2SO_4 solution at 25°C in the absence and presence of different concentrations of fenugreek extract. Parameters obtained from the polarization curves are listed in Table 4. These include anodic (β_a) and cathodic (β_c) Tafel slopes, corrosion potential (E_{corr}), corrosion current density (j_{corr}), and the corresponding surface coverage (θ) and inhibition efficiency percent (η%) [36-38].

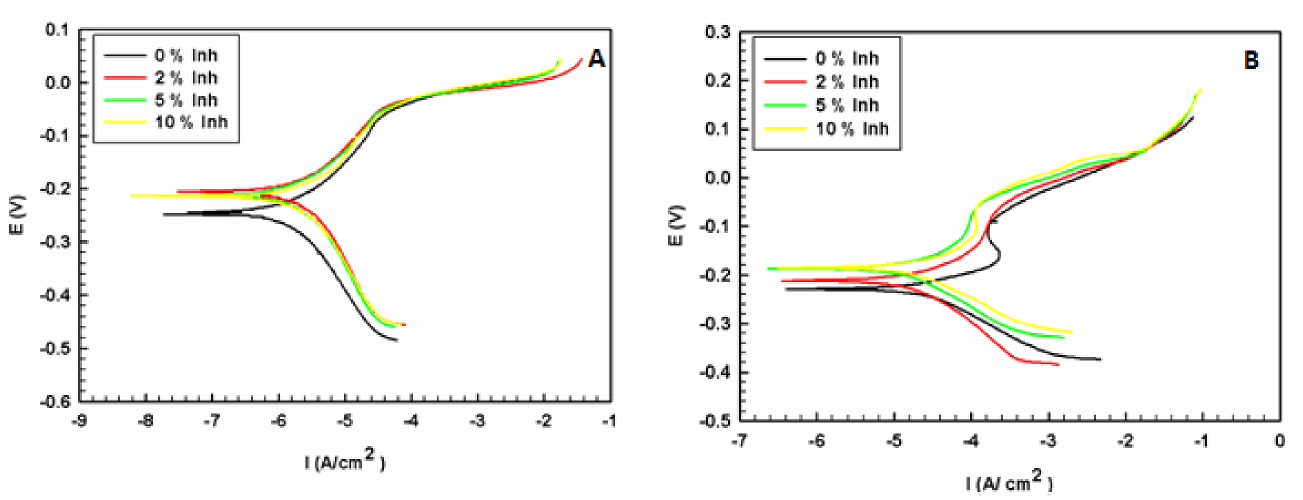

Figure 9. Linear polarization curves for (A) copper and (B) nickel electrodes in 2.0 M H_2SO_4 solution in absence and presence of different fenugreek extract concentrations at 25°C.

Table 4. Electrochemical parameters obtained from linear polarization measurements and corresponding surface coverage and inhibition efficiency values for copper and nickel in 2.0 M H_2SO_4 solution in absence and presence of different fenugreek extract concentrations at 25°C.

Copper						
[Inhibitor] (mL/L)	I_{corr} (μA/Cm^2)	E_{corr} (mV)	β_a (mV/dec)	β_c (mV/dec)	θ	η%
0	1.55	-244.97	121.51	173.12	-	-
20	0.34	-205.12	19.87	23.14	0.78	77.79
50	0.26	-211.26	24.43	21.54	0.83	82.94
100	0.25	-212.80	15.91	24.32	0.84	83.81
Nickel						
0	30.00	-228.71	68.82	92.79	-	-
20	13.90	-211.60	50.85	73.42	0.54	53.94
50	12.90	-185.99	47.93	74.27	0.57	57.05
100	7.00	-184.60	15.33	31.31	0.77	76.73

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 (E_{corr}) shift to more positive values in presence of the inhibitor indicating that the inhibitor has a stronger effect on the anodic metal dissolution than on the oxygen cathodic reduction. Thus, fenugreek can be considered as a mixed inhibitor that acts preferably on the anodic sites [8] 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 both metals surfaces does not affect the corrosion mechanism. The inhibition efficiency (η%) values increases by increasing the inhibitor concentration, the obtained values agree well with those obtained by gravimetric measurements, Table 1.

3.5.2. EIS measurements

The effect of fenugreek extract concentration on the impedance spectra, Bode and Nyquist plots, of copper and nickel electrodes in 2.0 M H_2SO_4 solution at 25°C is shown in Fig.10.

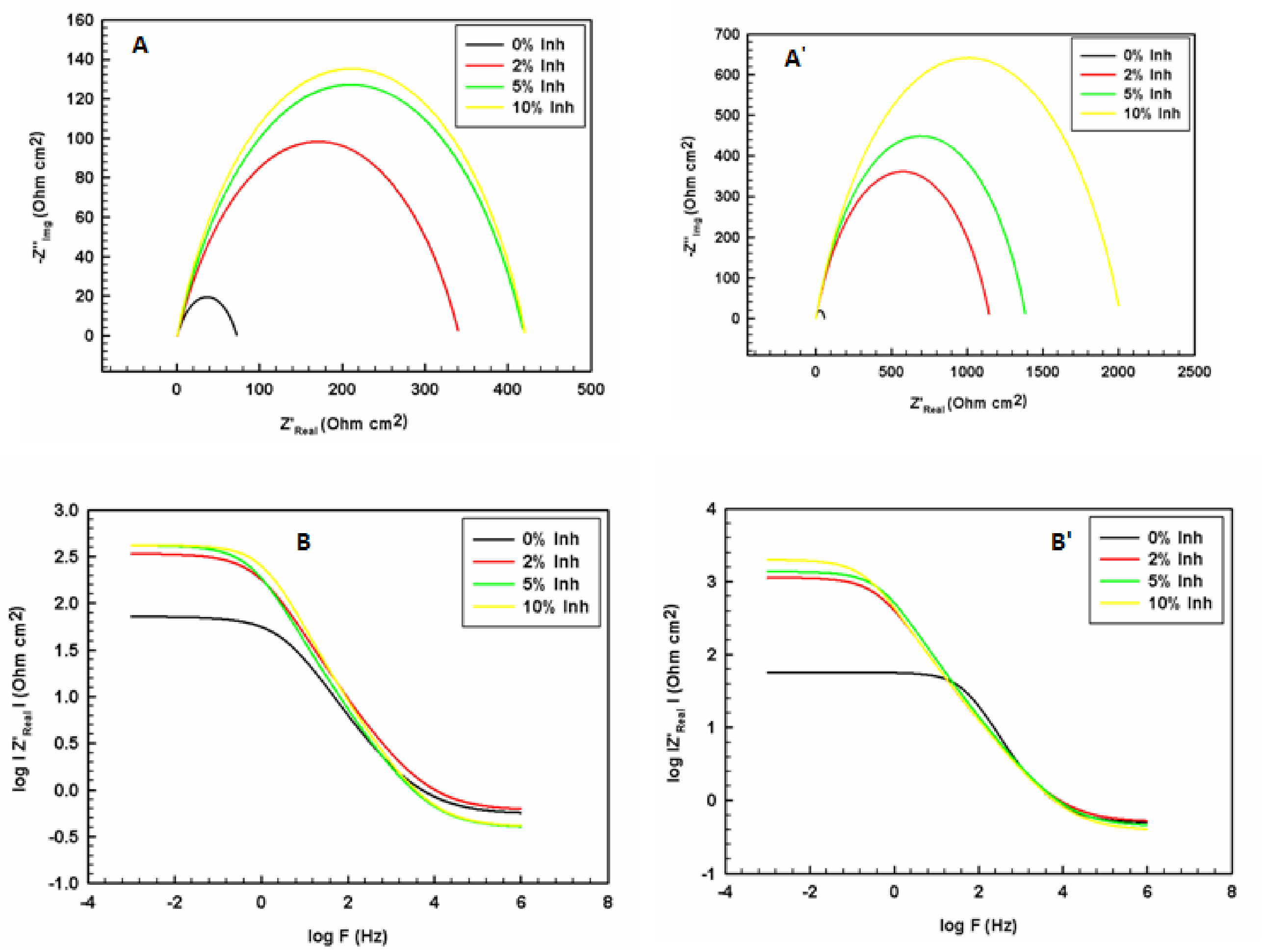

Figure 10. (A,A') Nyquist and (B,B') Bode plots for (A) copper and (B) nickel electrodes in 2.0 M H_2SO_4 solution in absence and presence of different fenugreek extract concentrations at 25°C.

Nyquist plots consist of a capacitive loops thus, copper and nickel corrosion in uninhibited and inhibited H_2SO_4 solution is charge transfer controlled. The addition of the inhibitor 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 was fitted by using the electrical equivalent circuit showed in Fig.11. The equivalent circuit consists of a constant phase element (CPE) in parallel with a charge-transfer resistance (R_{ct}). This CPE was used, rather than a capacitor component, to indicate the impedance behavior of the electrical double layer more accurately.

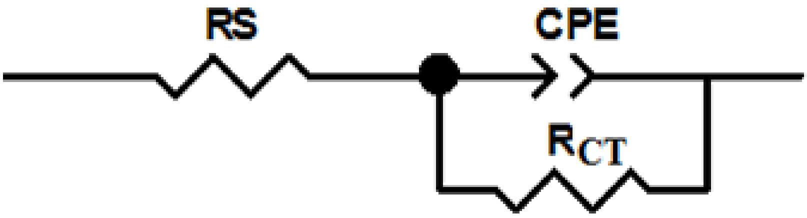

Figure 11. Electrical equivalent circuit used for fitting impedance data for (A) copper and (B) nickel electrodes in 2.0 M H_2SO_4 solution at 25°C.

The impedance parameters obtained by fitting the Nyquist plots and the calculated [39, 40] surface coverage (θ) and inhibition efficiency percent (η%)are listed in Table 5.

Table 5. Impedance data obtained from Nyquist plots and corresponding surface coverage and inhibition efficiency values for copper and nickel in 2.0 M H_2SO_4 solution in absence and presence of different fenugreek extract concentrations at 25°C.

Copper						
[Inhibitor] (mL/L)	R_S (Ω cm^2)	CPE × 10^2 (F cm^{-2})	n	R_{CT} (Ω cm^2)	θ	**η %**
0	0.56	17.4	0.63	75.31	-	-
20	0.62	8.23	0.66	373.20	0.80	79.82
50	0.40	8.12	0.69	467.80	0.84	83.90
100	0.41	4.90	0.72	476.20	0.84	84.18
Nickel						
0	0.43	4.11	0.70	598.80	-	-
20	0.54	3.55	0.71	1154.00	0.55	54.61
50	0.46	2.74	0.73	1457.00	0.59	59.21
100	0.41	2.33	0.72	2168.00	0.77	76.56

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 copper and nickel corrosion in H_2SO_4 medium. While, CPE values tend to decrease with increasing the inhibitor concentration due to the increased double layer thickness as a result of the inhibitor adsorption [40].

4. CONCLUSION

- Fenugreek extract can be used as a green corrosion inhibitor for copper and nickel in H_2SO_4 solution with a maximum efficiency values of 85.6% and 83.5% at immersion times of 24 and 48 h, respectively and by using 20 % (V/V%) of the extract.
- The adsorption of fenugreek extract on both metals obeys Langmuir adsorption isotherm. Florry-Huggins isotherm can applied successively only for nickel.
- Calculated thermodynamics parameters suggest that fenugreek extract is a good inhibitor for copper and nickel corrosion in H_2SO_4 solution.
- The decreased corrosion current and increased charge transfer resistance measured by linear polarization and EIS measurements, respectively, reflects the inhibition ability of fenugreek for copper and nickel corrosion in H_2SO_4 solution.

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