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FENNEL (*FOENICULUM VULGARE MILL*) SEEDS EXTRACT AS GREEN INHIBITOR FOR ALUMINIUM CORROSION IN HCl ACID SOLUTION: THERMODYNAMIC, ADSORPTION AND KINETIC STUDY

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ABSTRACT
The corrosion inhibition of aluminium in HCl solution by Fennel seeds (*Foeniculum vulgare* Mill**)** extract as a green inhibitor has been studied using weight loss, temperature effect and kinetic study methods. As inhibitor concentration increases corrosion rate decreases while percentage of inhibition efficiency (I.E.) increases. Corrosion rate increases with the increase in temperature. Mechanism of inhibition was also investigated by calculating the thermodynamic and activation parameters like (ΔG), (Q_{ads}), (E_a), (ΔH_{ads}) and (ΔS_{ads}). Physisorption of extract is best described by the Langmuir adsorption model. Maximum I.E. of Fennel seed extract was found up to 92.01 % at 1.2 g/L inhibitor concentration in 0.75 M HCl solution. Present study indicates that Fennel seeds extract is a good eco-friendly inhibitor for the corrosion of aluminium in HCl medium.

KEYWORDS: Corrosion, Aluminium, HCl, Fennel seeds extract, Weight loss.

1. INTRODUCTION
Corrosion is a huge problem whose economic consequences are disastrous and invaluable. Aluminium is the second metal most used after iron, on an industrial scale[1], considering diversified advantages, such as low cost, light weight and good thermal and electrical conductivity.[2] However, during service, aluminium-based components come in contact with some aggressive solutions such as hydrochloric acid, where they are used for acid pickling of aluminium, cleaning of oil refinery equipment and for chemical and electrochemical etching.[3] The use of inhibitors is one of the most practical options to protect metal from corrosion. Generally, organic and inorganic compounds are usually added to acid as corrosion inhibitors. Since most of these compounds are toxic, nonbiodegradable and costly to synthesize, there is a growing demand to find the environmentally safe inhibitors. In attempt to find the eco-friendly corrosion inhibitors, there is a growing trend to use natural products such as plants, spices, vegetable peels, seeds etc, as a corrosion inhibitor. Seed extract of *Cuminum cyminum* (Jeera)[4] and Coriander[5] has been used for prevention of corrosion of aluminium in HCl media. Fennel (*Foeniculum vulgare* Mill) belonging to the family Apiaceae (Umbelliferae) is native to central Europe and in the Mediterranean areas.[6] *F. vulgare* is a perennial herb (up to 40 cm high) with feathery leaves (up to 40 cm long) and yellow flowers (umbels 5–15 cm wide). The fruit is a dry and grooved seed from 4–10 mm long. It is widely cultivated throughout the temperate and tropical regions of the world for its aromatic fruits, which are used as a culinary spice.[7] Mature fennel fruit and its essential oil are used as flavoring agents in food products such as liqueurs, bread, pickles, pastries, and cheese. They are also used as a constituent in cosmetic and pharmaceutical products.[8,9] *F. vulgare* has shown antimicrobial[10], antioxidant activity[11], anti-inflammatory activity[12], antidiabetic activity.[13] The use of essential oils extracted from *F. vulgare* seed has been applied as green corrosion inhibitor for the corrosion of metals in hydrochloric acid solution.[14-21] The aim of the present study is to investigate the corrosion inhibition effect of Fennel seeds (Fig.1) as a cheap and environment friendly corrosion inhibitor for aluminium in various concentration of HCl medium by weight loss, effect of temperature and kinetic study methods.

2. MATERIAL AND METHODS
2.1 Preparation of sample and solution
The aluminium specimens with a chemical composition of 99.54 % Al, 0.090 % Si, 0.320 % Fe, 0.0012 % Cu, 0.0034 % Mn, 0.0014 % Mg, 0.0042 % Cr, 0.0046 % Ni, 0.0020 % Zn, 0.0079 % Ti, 0.0005 % Pb, and 0.0026 % Sn were used in the present study. The metal sheet, test

specimens of size 5.0 x 2.50 x 0.198 cm having an effective area of 0.2797 dm^2 were used. The specimens were cleaned by washing with distilled water, degreased by acetone, finally dried and weighted by using electronic balance. HCl acid was used as corrosive solution having concentration of 0.75, 1.0 and 1.25 M prepared by diluting analytical grade of HCl purchased from Merck using double distilled water.

2.2 Preparation of Fennel seeds extract

Fennel (*F. vulgare*) seeds were obtained from a local market in Surat, India. The seeds were collected and oven dried at 50° C then dried leaves are ground to powder form by using grinder. The solution of Fennel seeds extract (*F. vulgare*) was prepared by refluxing 5.0 gm of Fennel seeds powder with 100 mL of methanol for about 1 h and kept for 24 h, filtered and stored. The essential oils were dried over anhydrous sodium sulphate and then stored in sealed glass vials at 4 to 5°C prior to analysis. From this stock solution different concentrations of Fennel seed extracts solutions were prepared.

Fig. 1: Fennel seeds.

2.3 Weight loss measurements

Aluminium specimens having an area of 0.2797 dm^2 were each suspended in 230 ml of 0.75, 1.0 and 1.25 M HCl solution in absence and presence of 0.6, 0.8, 1.0 and 1.2 g/L concentration of Fennel seeds extract using glass hooks at 301± 1 K for an immersion period of 24h. After 24 h specimens were retrieved from beaker, washed with distilled water, dried well and reweighed. From the weight loss data, corrosion rate (CR) was calculated using following equation:

C.R. (mg/dm ^{2}d) = Weight loss (gm.) x 1000 / area in dm^2 x day...(1)

Inhibition efficiency (I.E.) was calculated by using following equation,

$$\mathrm{I.E.}\ (\%) = \left\{\frac{(W_u - W_i)}{W_u}\right\} \times 100 \qquad ...(2)$$

Where, Wu = Weight loss in absence of inhibitor, Wi = Weight loss in presence of inhibitor.

The degree of surface coverage 'θ' of the aluminium specimen for different concentration of HCl solution have been evaluated by weight loss experiments using the following equation,

$$\theta = \frac{(W_u - W_i)}{W_i} \qquad ...(3)$$

2.4 Temperature effect

To study the effect of temperature on corrosion rate, aluminium specimens were completely immersed in 230 ml of 0.75 M HCl solution without and with different concentrations of Fennel seeds extract at 313, 323 and 333 K for 2h.

3. RESULTS AND DISCUSSION

3.1 Weight loss experiments

3.1.1. Effect of acid concentration: Results showed in Fig.2 indicates that as the acid concentration increases corrosion rate increases. Corrosion rate was 2195.20, 6163.74 and 8283.87 mg $dm^{-2}d^{-1}$ corresponding to 0.75, 1.0 and 1.25 M acid concentration respectively for an exposure period of 24 h at 301± 1 K.

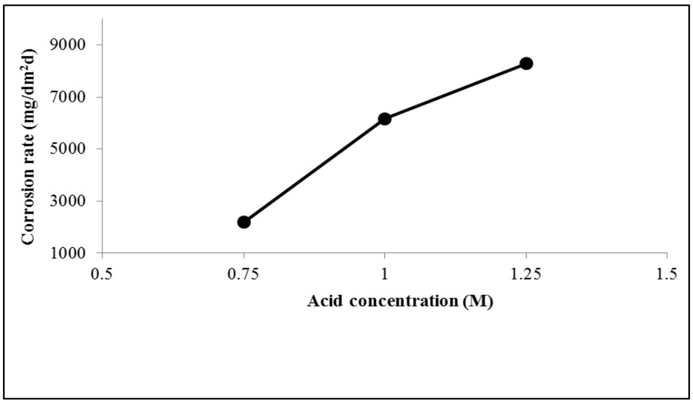


Fig. 2: Effect of acid concentration on corrosion rate of Al for 24 h immersion period at 301±1 K.

3.1.2. Effect of inhibitor concentration: At constant acid concentration, as the inhibitor concentration increases corrosion rate decreases (Fig. 3) while I.E. increases (Fig. 4). In 0.75 M HCl solution, the I.E. was found to be 59.12, 70.52, 82.89 and 92.01 % corresponding to 0.6, 0.8, 1.0 and 1.2 g/L inhibitor concentration respectively (Table-1).

Table 1: Inhibition efficiency (I.E.), Corrosion rate (ρ) and Surface coverage (θ) of Fennel seeds extract on Al in 0.75 M HCl for an immersion period of 24h at 301 ± 1 K.

Inhibitor	Inhibitor Concentration (g/L)	C.R. (ρ) (mg/dm^2d)	log ρ	I.E. (%)	Surface coverage (θ)	C/θ
Blank	-	2195.20	3.34	-	-	-
Fennel seed	0.6	897.39	2.95	59.12	0.59	1.016
	0.8	647.12	2.81	70.52	0.71	1.126
	1.0	375.40	2.57	82.89	0.83	1.204
	1.2	175.18	2.24	92.01	0.92	1.304

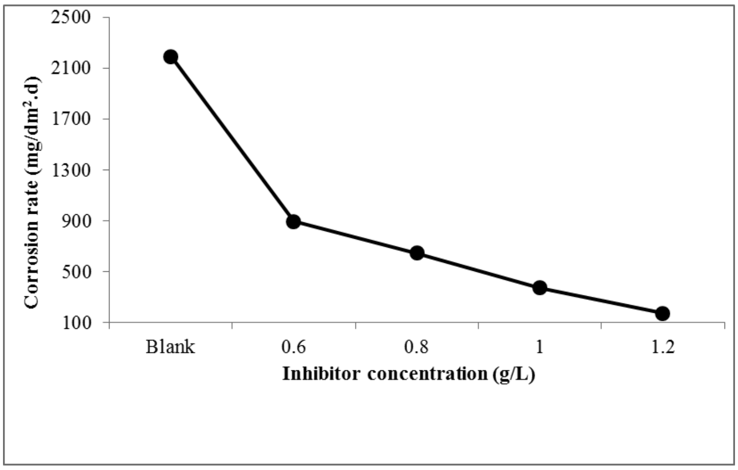


Fig. 3: Corrosion rate of Al in 0.75 M HCl solution in absence and presence of different concentration of Fennel seeds extract for an immersion period of 24 h.

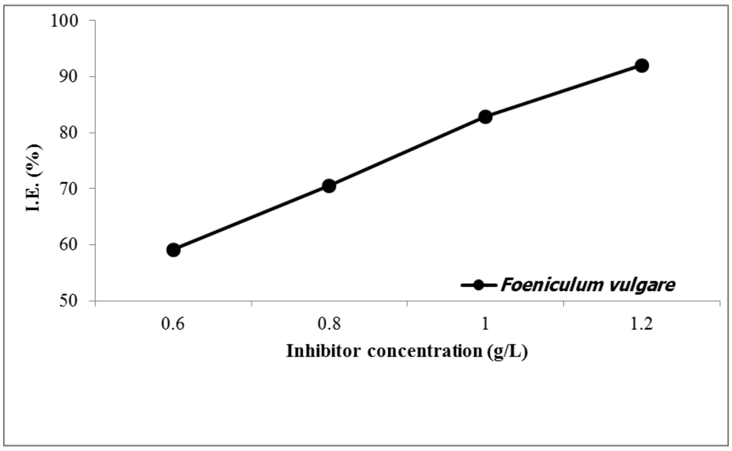


Fig. 4: Inhibition efficiency (I.E.) of Al corrosion in 0.75 M HCl solution in presence of different concentration Fennel seeds extract for an immersion period of 24 h.

3.2 Temperature effect

To investigate the influence of temperature on corrosion of aluminium, the weight loss experiments were also carried out at 313, 323 and 333 K temperatures in 0.75 M HCl in absence and presence of Fennel seed extract for an immersion period of 2h. Result in Table-2 shows that corrosion rate increases with rise in temperature. Corrosion rate was 21451.44, 26642.76 and 43417.92 mg/dm^2d corresponding to 313, 323 and 333 K respectively. Corrosion loss increases with temperature may be due to the desorption of the adsorbed molecules inhibitor and/ or aggressive at higher temperature and thus exposing the fresh metal surface to further attack[22],which results in intensification of the kinetic of electrochemical reaction[23] and thus explains the higher corrosion rate at elevated temperature. The addition of fennel seed extract in corrosive media indicates that as the temperature increases I.E. decreases (Table-2).

Table 2: Temperature effect on corrosion rate (CR), activation energy (E_a) and heat of adsorption (Q_{ads}) for aluminium in 0.75 M HCl in absence and presence of Fennel seeds extract for an immersion period of 2 h.

Inhibitor concent-ration (g/L)	Temperature 313 K		323 K		333 K		Mean (E_a) From Eq. (4) (kJ/ mol)	Qads (kJ/ mol)	
	CR mg/dm^{2}d	I. E. (%)	CR mg/dm^{2}d	I. E. (%)	CR mg/dm^{2}d	I. E. (%)		313-323 K	323-333 K
Blank	21451.44	-	26642.76	-	43417.92	-	23.39	-	-
0.6	9309.96	56.59	14115.12	47.02	24411.84	43.77	41.98	-32.10	-11.91
0.8	7336.32	65.80	12570.60	52.81	21108.24	51.38	45.80	-45.59	-05.37
1.0	6478.32	69.80	11240.52	57.81	18834.36	56.62	46.24	-44.01	-04.38
1.2	5577.36	74.00	9224.16	65.37	15959.88	63.24	45.66	-34.81	-08.18

3.2.1. Energy of activation (E_a)

The value of energy of activation (E_a) has been calculated with the help of Arrhenius equation.[24]

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad ...(4)$$

where, ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively. Results given in Table-2, indicates that the values of E_a were higher in inhibited acid ranging from 41.98 to 46.24 kJ/mol than E_a value for uninhibited acid (23.39 kJ/mol) which indicates physical adsorption of the inhibitor on metal surface and the adsorption of inhibitor causes an increase in the E_a value of the process.[25] The values of E_a were also calculated from the slope of the Arrhenius plot of log ρ versus 1/T x 1000 (Fig. 5) which is in good agreement with the calculated values.

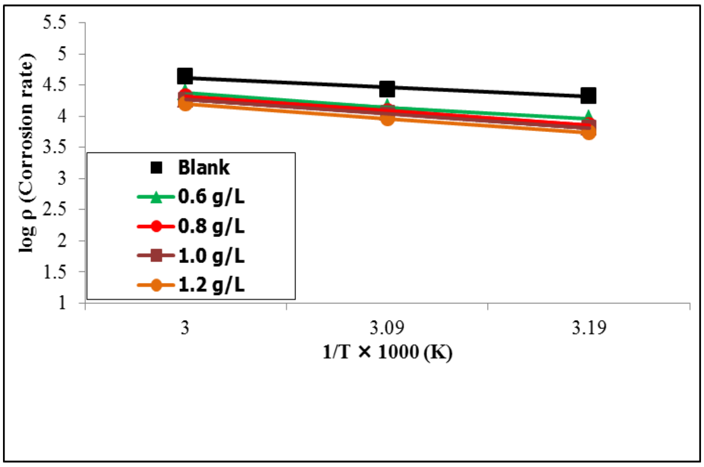


Fig. 5: Arrhenius plots for corrosion of Al in 0.75 M HCl in absence and presence of different concentration of Fennel seeds extract.

3.2.2 Heat of adsorption (Q_{ads})

The values of heat of adsorption (Q_{ads}) were calculated by using the following equation.[26]

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right]\left[\frac{T_1T_2}{T_2-T_1}\right] ...(5)$$

Where, θ_1 and θ_2 are the fraction of the metal surface covered by the inhibitor at temperature T_1 and T_2 respectively. It is evident that in all cases, the value of Q_{ads} were negative and ranging from -04.38 to - 45.59 kJ/mol. The negative values of Q_{ads} shows that the adsorption process and hence the I.E. decreases with rise in temperature supporting the physisorption mechanism.[27]

3.3.3. Adsorption isotherms: Adsorption isotherm study was conducted to investigate the interaction between the metal and inhibitor as well as the equilibrium of the adsorption. Basic information on the interaction between inhibitors and a metal surface can be provided using the adsorption isotherm.[28] Due to adsorption, inhibitor molecules block the reaction sites and reduce the rate of corrosion. The surface coverage 'θ' value was calculated by using equation-3. A plot of inhibitor concentration C_{inh} versus C_{inh}/θ was presented in Fig. 6 which gives straight line with slope values equal to unity indicates that the system follows Langmuir adsorption isotherm.[29] This isotherm can be represented as,

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad ...(6)$$

Where, K_{ads} is the equilibrium constant and C_{inh} is the inhibitor concentration.

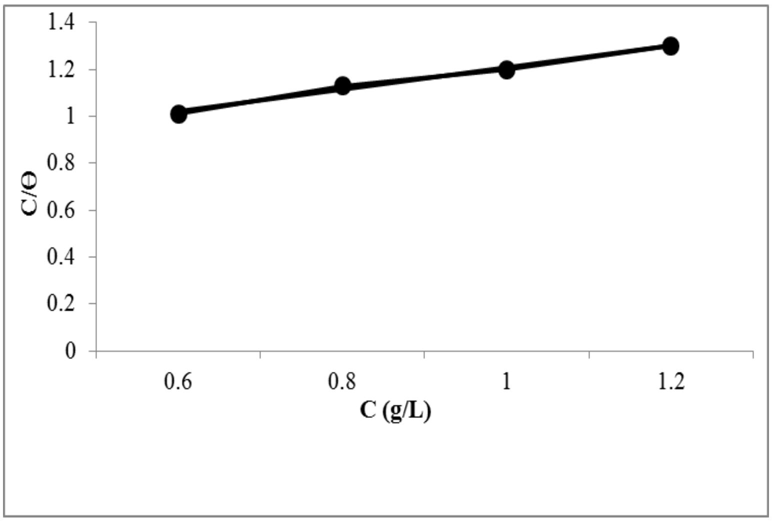


Fig. 6: Langmuir adsorption isotherm plot for Al in 0.75 M HCl containing Fennel seeds extract as green inhibitor at 301 K.

Table-3: Thermodynamic parameters of Al in 0.75 M HCl in absence and presence of Fennel as an inhibitor.

Inhibitor	**Inhibitor Concent-ration (g/L)**	**Free energy of adsorption (ΔG^o_{ads})**				**ΔH_{a°**		**ΔS_{a°**	
		313 K	**323 K**	**333 K**	**Mean**	**313 K**	**323 K**	**313 K**	**323 K**
Blank	0.0	-	-	-	-	23.20	18.29	-	-
Fennel seed	0.6	-10.60	-10.94	-11.28	-10.94	32.37	46.30	0.148	0.177
	0.8					42.65	43.66	0.171	0.169
	1.0					43.71	43.47	0.174	0.168
	1.2					39.68	46.34	0.161	0.177

3.3.4. Free energy of adsorption (ΔG^o_{ads})

'ΔG^o_{ads}' was determined by the Langmuir isotherm was given by a plot of C/θ versus C (Fig. 5). From the intercepts of the straight line on the C/θ axis, K_{ads} can be calculated which was related to ΔG^o_{ads} as given by the following equation:[30,31]

$$\Delta G^o_{ads} = -RT \ln (55.5\ K_{ads}) \quad ...(7)$$

Where, R is the gas constant, T is the concentration of water in solution in Molar[32], K_{ads} is the equilibrium constant of the adsorption/desorption process. The mean ΔG^o_{ads} value was negative (-10.94 kJ/mol) indicating that the adsorption mechanism of Fennel seeds on aluminium in 0.75 M HCl at the studied temperatures is physisorption with adsorptive layer having electrostatic character.[33] This is concluded on the fact that the values of ΔG^o_{ads} -20 kJ/mol are consistent with physisorption, while those around -40 kJ/mol or higher are associated with chemisorptions.[34]

3.3.5. Enthalpy of adsorption (ΔH°ads)

ΔH^o_a was calculated using the equations (8)

$$\Delta H^o_a = E_a - RT \quad (8)$$

Results indicates in Table-3 that values of ΔH^o_a were positive and increase in presence of inhibitor indicating a higher degree of surface coverage and higher protection efficiency attained due to raising the energy barrier for the corrosion reaction to occur.[35] The enthalpy change ΔH^o_a was positive and ranging between 32.37 to 46.34 kJ/mol indicating the endothermic nature of the reaction suggests that higher temperature favours the corrosion process.[36]

3.3.6. Entropy of adsorption (ΔS°ads)

ΔS^o_a[37] were calculated using the equations (9).

$$\Delta S^o_a = \Delta H^o_a - \Delta G^o_a / T \quad (9)$$

Positive values of ΔS°a ranging from 0.148 to 0.177 kJ/mol indicates that corrosion process is entropically favourable.[38]

3.4 Kinetic parameters: Rate constant (k) and Half-life ($t_{1/2}$)

As concentration of inhibitor increases rate constant k decreases whereas the half-life increases. This result was in good agreement with the result obtain by Talati and Modi.[39] Corrosion rate constant 'K' increases with increases in concentration of acid (Table-4). The values of half-life ($t_{1/2}$) were calculated by using the following equation:[40]

$$t_{1/2} = 0.693 / k \quad ...(10)$$

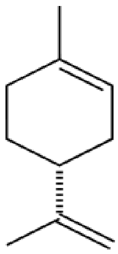
Where, 't' is time in hours and 'k' is rate constant.

Table 4: Kinetic data for the corrosion of Al in various concentration of HCl containing Fennel seeds extract.

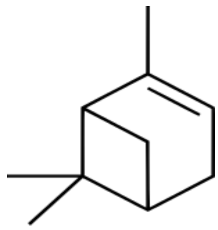
Inhibitor	Inhibitor concentration (g/L)	Acid concentration					
		0.75 M		1.0 M		1.25 M	
		Rate const. ($k\times10^{-3}$) (day^{-1})	Half life ($t_{1/2}$) (day)	Rate const. ($k\times10^{-3}$) (day^{-1})	Half life ($t_{1/2}$) (day)	Rate const. ($k\times10^{-3}$) (day^{-1})	Half life ($t_{1/2}$) (day)
Blank	0.0	99.48	07.00	307.53	02.25	439.41	1.57
Fennel Seeds	0.6	39.08	17.73	145.67	04.75	240.18	02.88
	0.8	27.98	24.76	106.42	06.51	166.34	04.16
	1.0	16.16	42.88	79.54	08.71	146.92	04.71
	1.2	07.52	92.15	62.45	11.09	113.59	06.10

3.5 Mechanism of corrosion inhibition by Fennel seeds extract

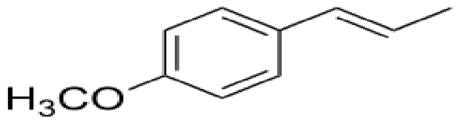
Phytochemical analysis of F. vulgare showed the presence of terpenes, alkaloids, flavonoids, tannins, and saponins. The major constituent of fennel oil is anethole. Other constituents include α-pinene, β -myrcene, βpinene, bitter fenchone, camphene, estragole (methylchavicol), fenchone, limonene, p-cymene, and safrole.[9,41-42] The adsorption of the inhibitor molecules on the aluminium surface is due to the donor acceptor interaction between pi-electrons of donor oxygen atoms and aromatic rings of inhibitor and the metal surface atom. The presence of -OCH3 group (i.e. an electron donating effect) will enhance the electron density by their inductive or mesomeric effect.[43] Structure of the main constituents of Fennel seed extract is given in Fig. 7.



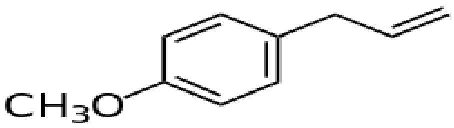
Limonene
M.F. - $C_{10}H_{16}$



β-pinene
M. F. - $C_{10}H_{16}$



Anethole
M.F. - $C_{10}H_{12}O$



Estragole
M.F. - $C_{10}H_{12}O$

Fig. 7: Structure of main phytoconstituents of Fennel seed extract.

Due to the complex nature of adsorption and inhibition of a given inhibitor, it is impossible for single adsorption mode between inhibitor and metal surface. Since there are many chemical constituents in fennel so they may inhibit the aluminium surface due to the synergistic effect of various molecules.[14,44-46]

4. CONCLUSIONS

On the basis of the study the following conclusions can be drawn:

1. The inhibitory action of Fennel seeds decreased when the temperature increases.
2. I. E. increases with an increase in Fennel seeds extract concentrations in 0.75 M HCl but decreased with rise in temperature.
3. Maximum I.E. of Fennel seed extract was found up to 92.01 % at 1.2 g/L inhibitor concentration in 0.75 M HCl solution.
4. The corrosion process is inhibited by adsorption of the Fennel seeds extract on the aluminium surface following Langmuir adsorption isotherm.
5. The negative free energy of adsorption ΔG^o_{ads} indicates strong and spontaneous adsorption of the Fennel seeds extract on the Al surface.

6. The fennel seeds extract can act as a green inhibitor for Al corrosion in hydrochloric acid environments.

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