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Performance of Fenugreek (Trigonella foenum graecum) Seed Extract As Inhibitor On Mild Steel Under Corrosive Medium- A Statistical View

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Abstract: In this study the performance of fenugreek seed (*Trigonella foenum graecum*) aqueous extract–KI system as inhibitor on the corrosion of mild steel immersed in 2M hydrochloric acid were investigated by mass loss method, in the presence and absence of potassium iodide. The main chemical constituent of the fenugreek extract is., leucine, 4-hydroxyisoleucine, alanine argentine and L-tryptophan. Inhibition efficiency was found to increase with increasing concentration of inhibitor (5 mg/dm^3 to 30 mg/dm^3) for 48 hours at room temperature. In the presence of potassium iodide there exists a synergistic effect. Synergism parameters have been calculated to evaluate the synergistic effect. Analysis of variance (F-test) reveals that the synergistic effect existing between fenugreek (*Trigonella foenum graecum*) extract and potassium iodide is statistically significant[1].

Key words: Mild steel; Fenugreek seed extract; Corrosive medium; weight loss method, Synergistic effect, ANOVA.

Introduction

The research in field of corrosion inhibition has been addressed towards the goal of using cheap, effective biomasses at low environmental impact. Keeping these factors in mind, several naturally occurring compounds have been selected as corrosion Inhibitors in the corrosive medium The selected inhibitor is non toxic utilized in food, cheap easily available and effective also. This paper describes the investigation of low toxic easily biodegradable plants. It has been investigated that the corrosion inhibition efficiency of fenugreek seeds aqueous extract is greater in Hydrochloric acid. This may be due to the presence of wide variety of free amino acids viz., leucine, 4-hydroxyisoleucine, alanine argentine and L-tryptophan in fenugreek plant. Among nitrogen containing compounds: quinoline, aniline, ephedrine, narcotine, brucine, and stryctuine have shown good corrosion inhibition.

Experimental

Fenugreek seeds were washed with distilled water and dried in sunlight. Then it is powered with the help of a mixer. The resulting fine powder was stored in a sample bottle. Six different concentrations (5, 10, 15, 20, 25, 30, g/dm^3) of the extract were prepared with 2N hydrochloric acid solution and was used for all measurement. Mild steel metal (the percentage elemental composition was found to be, C(0.048%), Mn (0.335%), Si (0.029%), P(0.041%) ,S (0.025%), Cr (0.050%), Mo (0.016%), Ni (0.019%) and Fe (99.437%) having a surface

area of 5x1cm^2 were cut from a large sheet. The specimens were polished successively with emery sheets, degreased and dried. Distilled water and AR grade HCl were used for preparing solution[4]. The specimens in triplicate were immersed in 2 M acid solution containing various concentrations of the inhibitor for six hours at 30 ^{0}C. The specimens were removed washed with water and dried. The mass of the specimens before and after immersion was determined using an electronic digital balance.

The metal surface was dipped in 100 ml of 1M acid solution, stirred without and with various concentrations of the inhibitor with various concentrations (5, 10, 15, 20, 25, 30, g/dm^3) for desired interval of time (48 hours) at 30 ^{0}C. Synergism parameters was also noted in the presence and absence of potassium iodide under the same experimental conditions. The dissolution rates (mpy) were calculated by estimating the amount of mild steel surface dissolved in corrosive medium. The average mass loss of the three replicate measurements was calculated. Inhibitor efficiency (I.E.), corrosion rate and surface coverage (θ) were calculated from the weight losses of the specimens in the absence and presence of the inhibitor using the equations.

The corrosion rate for room temperature with various concentrations of inhibitor and various concentrations of anions was obtained from the following formula,

$$\text{C.R (mpy)} = \frac{436.095 \times 1000 \times W}{A \times T}$$

Where, W = Weight loss in grams, A = Area of specimen in cm^2 T = Exposure time in hours. The unit of the corrosion rate is in mills per year (mpy).

$$IE\% = \frac{[\text{Weight loss without inhibitor - weight loss with inhibitor}]}{\text{Weight loss without inhibitor}} x100$$

The corrosion rate was calculated by measuring the amount of mild steel dissolved in the solution analytically[2,3].

$$\text{Surfacecoverage } (\theta) = \frac{\text{Weightloss without inhibitor} - \text{weight loss withinhibitor}}{\text{weight loss without inhibitor}}$$

Synergism parameters[5] : Synergism parameters are indications of the synergistic effect existing between two inhibitors. Synergism parameters were calculated using the relation

$S\theta = 1 - \theta_{1+2} / 1 - \theta'_{1+2}$ where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \times \theta_2)$, being θ_1 = surface coverage of substance 1 and θ_2 = surface coverage of substance. θ'_{1+2} = combined surface coverage of substances 1 and 2. If synergistic effect exists between the inhibitors, Sθ value will be greater than 1.

Analysis of variance (F-Test)

An F-test was carried out to investigate whether the synergistic effect existing between inhibitor systems is statistically significant. If F-value is greater than 4.96 for 1,11degrees of freedom, the synergistic effect proves to be statistically significant. If it is less than 4.96 for 1, 11 degrees of freedom, it was statistically significant at 5% level of significance[4].

Result and discussion

Mass loss of mild steel in 2 M HCl was determined in the absence and presence of the tested extract. The data in Table (1) show the effect of concentration of different concentration of the extract on the percentage inhibition and indicate that by increasing the concentration of the extract, the % efficiency increases. This indicates that the fenugreek extract behave as inhibitors over the concentration range studied.

Table1. Effect of inhibitor concentrations on the percentage inhibition efficiency of mild steel in 2 M HCl solution from mass loss method at 30°C.

Inhibitor	Concentration (g/dm3)	Weight loss (g)	I.E. (%)	Surface coverage (θ)	Corrosion rate (mpy)	C/(θ)
Fenugreek seeds extract	**Blank**	0.3421	-	-	59675.24	-
	5	0.2541	25.72	0.26	44324.70	19.44
	10	0.2321	32.15	0.32	40487.06	31.10
	15	0.2111	38.29	0.38	36823.86	39.17
	20	0.176	48.55	0.49	30701.09	41.19
	25	0.1578	53.87	0.54	27526.32	46.41
	30	0.1462	57.26	0.57	25502.84	52.39

Adsorption isotherm: Assuming the corrosion inhibition was caused by the adsorption of the fenugreek extract, and the values of surface coverage for different concentrations of inhibitors in 2M HCl were evaluated from mass loss measurement[6,7]. From the values of (θ), it can be seen that the values of (θ) increased with increasing the concentration of fenugreek extract. Using these values of surface coverage, the best fit was obtained using the Langmuir isotherm. The Temkin adsorption isotherm was applied to investigate the adsorption mechanism, by plotting (θ) vs log C, a straight line was obtained (Fig.1). This implies that the adsorption of fenugreek extract on mild steel, in 2M HCl solution, obeys Langmuir's adsorption isotherm principle which means there is no interaction between the adsorbent molecules at the surface of mild steel. The expression used was for Langmuir isotherm; $\theta / (1- \theta) = KC$ and $C/ \theta = 1/K_{ads}+C$ and Freundlich adsorption isotherm: $\theta = K_{ads} C$, where C= conc. of inhibitor; θ = surface coverage.

Figure1. Langmuir and Freundlich isotherm for adsorption of Fenugreek extract onto mild steel surface in 2M HCl.

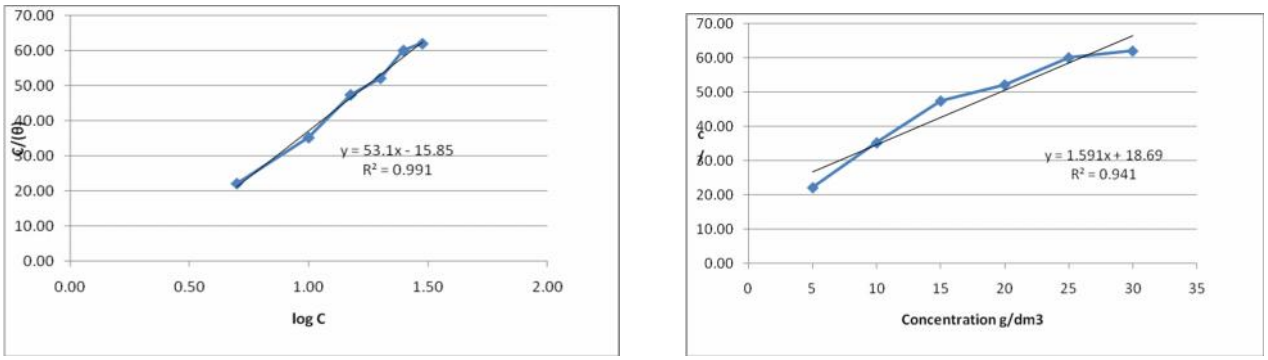

Table (4) shows the calculated thermodynamic parameters. Calculated values of activation energy Ea ($kJmol^{-1}$), Rate constant, k (s^{-1}) and Half life (s) for mild steel at 30 ^{0}C are recorded in table-2. These values indicate that the adsorption of fenugreek extract on the surface of mild steel is spontaneous and favored the mechanism of physical adsorption.

Table 2. Calculated values of activation energy Ea ($kJmol^{-1}$), Rate constant, k (s^{-1}) and Half life (s) for mild steel at 30 ^{0}C.

Inhibitor with corrosive media	slope	R^2	Ea	Rate constant	Half life ($t_{½}$)
HCl	0.781	0.949	9.495	0.02544	27.24

As seen from Table (1), the percentage inhibition efficiency of the tested extract is low, so in order to increase these values we use different concentrations of potassium iodide. Table (3) shows the % IE of the investigated extract in presence of various concentrations of potassium iodide.

Table-3 Data from mass- loss of zinc dissolution in 2 M HCl at different concentrations of the fenugreek seeds extract with addition of various concentrations of KI at 30^{o}C-2 days duration

Concentration Fenugreek seeds extract (g/dm3)	**Concentration of potassium Iodide (M)**						
	0.01	**0.02**	**0.03**	**0.04**	**0.05**	**0.06**	**0.07**
	IE (%)						
Blank	-	9.38	11.14	12.89	25.75	26.05	12.90
5	25.72	32.48	31.89	68.17	68.58	69.77	67.42
10	32.15	35.40	35.98	69.01	69.60	70.48	68.39
15	38.29	42.71	45.92	54.98	58.20	64.34	71.94
20	48.55	51.77	54.98	71.32	75.12	74.57	72.26
25	53.87	61.41	64.05	77.65	81.50	79.25	77.10
30	57.26	64.63	64.63	85.65	79.60	77.14	75.16

It is found that as the immersion period increase, the inhibition efficiency decreases (table -4). The inhibition efficiency for the given formulation of 2 M HCl + 30 g/dm3 Fenugreek extract + 0.06 M KI offered 81.50 % in 48 hours duration and decreased to 76.32 % on 10th day. This may be due to formation of porous complex in presence of 2 M HCl.

Table-4 Influence of immersion of the IE of Fenugreek extract-KI system

Immersion period	**2**	**4**	**6**	**8**	**10**
	2 M HCl + 30 g/dm3 Fenugreek extract + 0.06 M KI				
Weight loss	0.0633	0.0635	0.0657	0.077	0.081
Corrosion rate (mpy)	11041.93	11076.81	11460.58	13431.73	14129.48
Inhibition efficiency (%)	81.50	81.44	80.80	77.49	76.32

Synergism parameters (Sθ): Synergism parameters have been used to confirm the synergistic effect existing between two fenugreek extract and potassium iodide. Synergism parameters have been calculated for fenugreek extract and potassium iodide (0.01 M to 0.07M) systems. The results are given in Table5. It is observed that the synergism parameters are greater than 1. This confirms the synergistic effect existing between fenugreek extract and potassium iodide. It is also interesting to note that the values of Sθ are slightly smaller in the case of 0.07 M of KI when compared to the other combinations. This is in agreement with the inhibition efficiencies obtained by weight loss method. Thus the values of synergism parameters give a quantitative value of synergism existing between fenugreek aqueous seed extract and potassium iodide. Thus the increase in IE % caused by KI and fenugreek aqueous seed extract is due to the synergistic effect[5].

Table 5. Synergism parameter (Sθ) derived from inhibition efficiencies of Fenugreek extract-KI system

Fenugreek seed extract (mg/dm3)	Potassium Iodide(M)											
	0	**0.01**	**Sθ**	**0.02**	**Sθ**	**0.03**	**Sθ**	**0.04**	**Sθ**	**0.05**	**Sθ**	**0.06**	**Sθ**
0	0	5	-	11	-	13	-	26	-	25	-	13	
5	0	9.4	6.5	32	8.0	68	4.6	69	2.0	26	2.5	67	0.6
10	26	33	7.6	36	8.8	69	5.6	70	2.5	70	2.8	68	0.8
15	32	35	7.5	46	8.2	58	7.8	58	2.9	71	2.8	71	1.2
20	38	42	8.0	60	8.1	75	7.8	75	2.4	64	2.4	72	1.1
25	49	51	7.3	64	8.2	82	7.7	82	1.9	75	2.3	77	1.0
30	53	61	7.3	65	8.7	77	8.8	77	2.1	79	2.5	75	1.3

Analysis of variance (ANOVA): To investigate whether the influence of KI on the inhibition efficiencies of fenugreek extract is statistically significant, F-test was carried out. The results are given in Table-6. The results of Analysis of Variance (ANOVA) shows the influence of 0.01,0.02,0.03,0.04,0.05,0.06 and 0.07 M of potassium iodide on the inhibition efficiencies of 5,10,15, 20, 25 and 30 g/dm3 of fenugreek aqueous seed extract. The obtained F-value 5,10,15 and 30 g/dm3 of fenugreek aqueous seed extract was not statistically significant, since it was less than the critical F-value 4.96 for 1, 11 degrees of freedom at 5 % level of significance. Therefore, it is concluded that the influence of 20 and 25 g/dm3 fenugreek aqueous seed extract on the inhibition efficiencies of various concentrations of potassium iodide is statistically significant[4,8].

Table-6 ANOVA statistics for all inhibition results based on comparison of synergism

Fenugreek seed Extract (mg/dm3)	Source Of Varience	Sum Of Squares SS	Degree Of Freedom df	Mean Square MS	Degree of Variance (F)	Level Of Significance 5 % =4.96
5	between	0.035650	1	0.0357	0.0001	
	within	2970	11	270.0637		NS
10	between	5.97	1	5.97	0.0213	NS
	within	3078	11	279.78		
15	between	1290	1	1290	3.3499	NS
	within	4237	11	385		
20	between	1665	1	1665	6.2220	S
	within	2945	11	267.73		
25	between	18601	1	1860	7.1573	S
	within	2859	11	259.9		
30	between	1665.8	1	1666	4.3146	NS
	within	4247	11	386.09		

S: Significant, NS: Not Significant

Conclusions

The inhibition efficiency (IE) of fenugreek aqueous seed extract –KI system in controlling corrosion of mild steel in 2 M hydrochloric acid solution has been evaluated by weight loss method. The study reveals that the formulation consisting of 25 mg/dm3 of fenugreek aqueous seed extract and 0.06 M of potassium iodide has 85% inhibition efficiency in controlling corrosion of mild steel immersed in an 2 M hydrochloric acid solution for 48 hours duration. Synergistic parameters suggest that a synergistic effect exists between fenugreek aqueous seed extract and potassium iodide.

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