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## Natural Fenugreek Seeds as an Eco-Friendly Corrosion Inhibitor for Steel in Aqueous Solutions

A.S.Fouda<sup>1,\*</sup>, H.M.El-Abbasy<sup>2</sup> and A.H.Badr<sup>3</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura- 35516, Egypt,

<sup>2</sup>Higher Institute of Egypt for Engineering and Technology, Mansoura, Egypt.

<sup>3</sup> Lab Manager in Talkha Station at Water and Wastewater Daqahlia Company, Egypt.

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### ABSTRACT

The influence of a natural extract of fenugreek on the corrosion of steel in 10 ppm NaCl and 35 ppm  $Al_2(SO_4)_3$  has been studied by weight loss, polarization and EIS measurements. Results obtained show that the natural substance inhibits the corrosion process. It acts on the cathodic domain without modifying the reduction mechanism. The inhibition efficiency increases with fenugreek concentration to attain 75 % at extract of 0.6 g/L of fenugreek at temperatures between 303 and 333K. The effect of temperature on the corrosion behaviour of steel indicated that inhibition efficiency is temperature dependent. The activation energy of adsorption is determined.

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## Introduction

The use of inhibitors is a practical technique to secure metals and alloys from aggressive environment. Large numbers of organic compounds revealed that N, S and O containing organic compounds may be efficient inhibitors. However, most of these compounds are not only expensive, but also toxic to living beings. It is needless to point out the importance of cheap and safe inhibitors of corrosion. So, considerable efforts are made to find corrosion inhibitors which are environmentally safe, ready available and of relatively low cost. Literature shows a growing trend in the use of natural products known as nontoxic compounds, called also green inhibitors, as corrosion inhibitors. We cited green tea [1], propolis [2], halfa barr [3]. A part of the program of our laboratory is devoted to research new non-toxic inhibitors. Natural plants are added as extract, oil or pure compounds and are the subject of various contributions: limonene [4], ginger [5], henna [6], jojoba oil [7], rosemary oil [8], artemisia oil [9], bgugaine [10-12], thym [13], eugenol and acetyleugenol [14], pulegone [15], menthols [16], cedar [17], rosmarinus [18], pulegone [19], have been found to be very efficient corrosion inhibitors for metal in aggressive media. Our choice is made on fenugreek seeds, which contain the unique major free amino acid 4-hydroxyisoleucine (4-OH-ILeu) [20], to test as a non-toxic inhibitor for the protection of steel against corrosion in acid media.

The aim of the present paper is to study by gravimetric, polarization and EIS measurements, the effect of the extract of the natural substance fenugreek as a non-toxic compound, on the corrosion of steel in 10 ppm NaCl and 35 ppm  $Al_2(SO_4)_3$  solution in the temperature range 303 - 333 K.

### Experimental

Tele:

The investigated steel materials of chemical composition in weight% of 0.13 C, 0.029 Si, 0.018 S, 0.0067 P, 0.397 Mn, 0.025 Ni, 0.0076 Cr, 0.0020 Mo, 0.0010 V, 0.036 Cu, 0.0010 Sn, 0.0057 Co, 0.126 Al, 0.023 Zn, 0.0020 Mg, 0.0046 Nb, and 0.0025 Bi, the rest Fe are used.

4-hydroxyisoleucine (2S,3R,4S)



Figure 1. Molecular structure of 4-hydroxyisoleucine (4-OH-ILeu)

The aggressive solution (10 ppm NaCl and 35 ppm  $Al_2$  (SO<sub>4</sub>)<sub>3</sub> solution) is prepared by dilution of 100 ppm NaCl and 1000 ppm  $Al_2(SO_4)_3$ . The fenugreek seeds were ground and dried. The inhibitory solutions are prepared from boiling aqueous extract containing 1g/L of fenugreek during 30 min and soaked all night.

The extract was filtered to serve as initial solution. Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume is 100 mL. The steel specimens used have a square form (2.0 x 1.8 x 0.1 cm). Prior to immersion, the steel samples are polished with different emery papers up 1000, degreased with acetone, washed thoroughly with doubly distilled water, and finally dried in air. The immersion time for the weight loss is 21 hours at 303K and the same time at other temperatures. Electrochemical measurements were carried out in a conventional three electrode electrolytic cylindrical Pyrex glass cell. The working electrode had the form of a disc cut from the steel sheet. The area exposed to the corrosive solution was 1 cm<sup>2</sup>. A saturated calomel electrode (SCE) and a platinum electrode were used, respectively as reference and auxiliary electrode. The temperature was thermostatically controlled at 298±1 K. Working electrode was repolarized at -1500 to +1000 mV and E<sub>corr</sub> were monitored until stationary (30 min). The scan rate was 1 mVsec<sup>-1</sup>.

The EIS spectra were recorded at open circuit potential (OCP) after immersion the electrode for 10 minutes in the test solution. The AC signal was 5 mV peak to peak and the

frequency range studied was between 100 kHz and 10 Hz. The impedance diagrams are given in the Nyquist representation. To ensure the reproducibility each experiment was repeated twice and the average values was taken.

All electrochemical experiments were carried out using Gamry instrument PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 Corrosion software, EIS300 electrochemical impedance spectroscopy software, EFM140 electrochemical frequency modulation software and Echem Analyst 5.5 for results plotting, graphing, data fitting and calculating.

## **Results and discussion**

## Gravimetric measurements

The corrosion rate in 10 ppm NaCl and 35 ppm  $Al_2(SO_4)_3$  ( $W^{\circ}_{corr}$ ) and at various concentrations of the tested extract ( $W_{corr}$ ) is determined after 21 hours of immersion at 303 K. Values of corrosion rate and inhibition efficiencies are given in Table 1. The inhibition efficiency IE is calculated by the relation:

% IE = 100 x 
$$[1 - (W_{corr} / W_{corr}^{\circ})]$$
 (1)  
where  $W_{corr}$  and  $W_{corr}^{\circ}$  are the corrosion rates of steel with and

without fenugreek It is clear that the addition of fenugreek reduces the corrosion rate ( $W^{\circ}_{corr}$ ) in 10 ppm NaCl and 35 ppm Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution. It is clear from Table 1 that  $W^{\circ}_{corr}$  decreases more and more with the increase of natural extract. This phenomenon is widely observed from the reduced quantity of hydrogen formed on the metal surface. The inhibitory effect increases then with the increase of fenugreek concentration to attain 75% at 0.6 g/L of fenugreek extract. From these essays at 303 K, we may conclude that fenugreek is an efficient inhibitor of steel corrosion in 10 ppm NaCl and 35 ppm Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution.

#### **Polarization Measurements**

Polarization essays were performed to know how inhibitory effect acted. Fig. 2 shows the influence of fenugreek extract on the polarization curves for the steel electrode in 10 ppm NaCl and 35 ppm  $Al_2(SO_4)_3$  solution. Values of associated electrochemical parameters and corresponding inhibition efficiencies (% IE) are given in Table 2. The examination of Fig. 2 and Table 2 shows that the addition of the fenugreek decreases both the cathodic and anodic current density. The decrease is more pronounced with the increase of the inhibitor concentration. The Tafel plots indicate that the mechanism of cathodic reduction is activation control.

The presence of the tested extract does not affect the cathodic Tafel slope, indicating that the mechanism of cathodic reduction is not modified with the fenugreek concentration. Also the corrosion potential is almost the same in the presence of extract. In the other hand in the anodic domain, a slight decrease of anodic current is observed in the presence of extract. The cathodic effect is then dominant against the anodic one. In other words, the decrease of the corrosion rate may be explained by the inhibitory action of the extract on cathodic branches of the polarization curves by blocking the cathodic reduction. The observed inhibitory action of fenugreek may be due to the adsorption of its molecules on the metal surface.

The inhibition efficiency reaches 65% at 0.6 g/L. In order to get more information about the corrosion behavior of steel in uninhibited acid and inhibited acid at different concentrations of natural extract, electrochemical impedance spectroscopy (EIS) measurements have been carried out at 298 K. Table 3 collects the EIS parameters and corresponding efficiency derived from EIS diagrams.



Figure 2. Polarization curves of steel in 10 ppm NaCl and 35 ppm Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub> at various concentrations of fenugreek EIS measurements

The charge-transfer resistance ( $R_{ct}$ ) values are calculated from the difference in impedance at lower and higher frequencies. Figure 3 shows the Nyquist plots for steel in 10 ppm NaCl and 35 ppm Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution with and without different concentrations of fenugreek seeds extract at 303 K.. The double layer capacitance ( $C_{dl}$ ) and the frequency at which the imaginary component of the impedance is maximal (- $Z_{max}$ ) are found as represented in equation:

 $C_{dl} = (1/\omega) R_{ct}$ (2) where  $\omega = 2\pi f_{max}$ . F<sub>max</sub> is the maximum frequency

The inhibition efficiency got from the charge transfer resistance is calculated by:

% IE = 100 [1 - (
$$R_{ct} / R_{ct/inh}$$
)] (3)

where  $R_{ct/inh}$  and  $R_{ct}$  are the charge transfer-resistance values with and without inhibitor, respectively. The increase of  $R_{ct}$  and the decrease of the capacitance with the concentration of extract can be explained by some decrease of the surface heterogeneity, due to the adsorption of the extract on the most active adsorption sites.

It is important to note that the IE values calculated using EIS method are larger than the values obtained by the other methods. This is due to the difference in the required conditions for each technique used. All the techniques used indicate that fenugreek extract give good inhibitive power for the corrosion of carbon steel.



Figure 3. Impedance plots for steel in 10 ppm NaCl and 35 ppm Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub> solution and with different concentrations of fenugreek

# Table 1.Weight loss of steel in 10 ppm NaCl and 35 ppm Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub>l at different concentrations of fenugreek and the corresponding inhibition efficiencies at 303 K after 21 h immersion

Fenugreek, Ppm	W <sub>corr</sub> mg cm <sup>-2</sup>	% IE
Blank	1.44	
100	0.960	33.3
200	0.720	50.0
300	0.570	60.4
400	0.490	66.0
500	0.430	70.1
600	0.360	75.0

 Table 2.Electrochemical parameters of steel in 10 ppm NaCl and 35 ppm Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub> + fenugreek extract at various concentrations and the corresponding inhibition efficiency

Conc. ppm	i <sub>corr</sub> , μA cm <sup>-2</sup>	-E <sub>corr</sub> , mV vs. SCE	β <sub>a</sub> , mV dec <sup>-1</sup>	$\beta_{c,}$ mV dec <sup>-1</sup>	CR mmpy	θ	% IE
Blank	149	570	205	88	1.74		
100	86	692	506	160	1.01	0.423	42.3
200	77	725	400	140	0.90	0.483	48.3
300	71	736	334	929	0.83	0.523	52.3
400	64	734	380	640	0.75	0.570	57.0
500	58	735	330	700	0.68	0.611	61.1
600	52	722	330	760	0.61	0.651	65.1

Table 3.Characteristic parameters evaluated from EIS diagrams for steel in 10 ppm NaCl and 35 ppm Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub>

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Conc. ppm	$\frac{R_{ct}}{\Omega cm^2}$	C <sub>dl</sub> , F cm <sup>-2</sup> x 10 <sup>-2</sup>	% IE
Blank	5.6	47.0	
200	24.9	19.1	77.6
300	56.2	14.9	90.0
500	76.8	7.6	92.7
600	127.6	5.2	95.6

Table 4. Effect of temperature on the % IE of C-steel at 0.1- 0.6g/L

(t = 12 h) different concentrations of fenugreek seeds extract

Conc., ppm	% IE					
Temp. °C	100	200	300	400	500	600
30	33.3	50.0	60.4	66.0	70.1	75.0
40	25.0	40.5	50.0	58.3	63.1	67.3
50	20.0	33.1	43.0	50.0	55.4	60.0
60	18.7	28.2	37.8	44.0	50.0	54.1

#### **Effect of Temperature**

Since temperature has a great effect on the corrosion rate and acid pickling of steel, usually carried out at elevated temperatures up to 333 K in 10 ppm NaCl and 35 ppm Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solutions, measurements were made in 303-333 K. Inhibitors are expected to be chemically stable to provide high protective efficiency in hot solutions. Gravimetric measurements are also taken at various temperatures 303-333K with and without inhibitor, during a period of 21h and at a different concentrations; the corresponding results are given in Table 4. It is clear from Table 4 that the inhibition efficiency decreases with the rise of temperature. This indicates that the extract was adsorbed physically on the metal surface and by raising the temperature the extract molecules desorbed from the metal surface. Figure.4 shows Arrhenius plots of the corrosion rate for both the blank and the inhibitor. The activation energies are determined by the relation:

$$k_{corr} = A \exp\left(-E_{a}^{*}/RT\right)$$
(4)

where  $k_{corr}$  is the corrosion rate in mg cm<sup>-2</sup> min<sup>-1</sup>,  $E_a^*$  is the activation energy, R is the universal gas constant, T is the absolute temperature in K

The activation energies are  $E_a^* = 10.2 \text{ kJ mol}^{-1}$  and  $E_a^* = 40.9 \text{ kJ mol}^{-1}$  are the activation energies in the absence and presence of fenugreek, respectively. The low value of the activation energy (less than 80 kJ mol<sup>-1</sup>) indicate physical adsorption of the extract molecules on metal surface.

The decrease of % IE with temperature is explained by the adsorption of an organic adsorbate on the surface of a metal is regarded as a substitutional adsorption process between the organic compound in the aqueous phase,  $\text{org}_{aq}$ , and the water molecules adsorbed on the electrode surface  $H_2O_{suf}$ . [21]

The addition of plants extracts led to an increase in the apparent activation energy to values greater than that of the uninhibited solution suggesting that higher energy barrier for the corrosion process in the inhibited solutions associated with physical adsorption or week chemical bonding between the inhibitor species and the steel surface [22-23].



#### Figure 4. Arrhenius plots as log k<sub>corr</sub> vs. 1/T for carbon steel in 10 ppm NaCl and 35 ppm Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the absence and presence of various concentrations of fenugreek

4-hydroxyisoleucine (the main component in the extract) may adsorb on the steel surface through the O and N atoms in its neutral form

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