

# Aqueous extracts for fenugreek leaves and seeds as green Inhibitors for mild steel corrosion in acidic solutions

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## Abstract

Electrochemical impedance spectroscopy and potentiodynamic polarization measurements were used to study the effect of aqueous extract of fenugreek leaves (AEFL) and aqueous extract of fenugreek seeds (AEFS) on the corrosion of mild steel in HCl and H<sub>2</sub>SO<sub>4</sub> solutions. In both acids, AEFL and AEFS act predominately as anodic type inhibitors.

The inhibition efficiency of both AEFL and AEFS increases with increasing of their concentration in 2.0 M of both acids, but at certain concentration of both extracts it decreases with increasing concentration of both acids. However, in HCl solutions, the inhibition efficiency of both AEFL and AEFS was always greater than in H<sub>2</sub>SO<sub>4</sub> solutions for otherwise identical conditions.

In HCl solutions the adsorption of both AEFL and AEFS on mild steel surface obeys the Langmuir adsorption isotherm, while obeys the Temkin adsorption isotherm in H<sub>2</sub>SO<sub>4</sub> solutions. It was found that the obtained results from EIS and PDP measurements are in good agreement. Good correlation between the inhibitor constituents and its inhibition efficiency in both acids was obtained and discussed.

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## Introduction

Corrosion of metals is a very common problem that has economic implications costing billions of dollars each year. Corrosion environment can be broadly classified as atmospheric, underground/soil waste, acidic, alkaline and combinations of these. A wide variety of acid or alkaline conditions are encountered in common environments. Many of the several corrosion problems encountered in the industries involves acids and in certain cases due to alkalis and solvents. Hence corrosion inhibition programs are now required in many industries such as oil and gas exploration and production, petroleum refining, chemical manufacturing and the product additive industries.

The corrosion inhibition is achieved by the addition of inhibitors to the system that prevent corrosion from taking place on metal surface. Inhibitors are chemicals that often work by adsorbing themselves on the metallic surface, protecting the metal surface by forming a film.

The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties [1-15]. Of these only very few are actually used in practice. This is partly due to the fact that desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability and environmental friendliness are of considerable importance in order to assess the current state of the art in the so called green chemistry. By definition, green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment.

Unfortunately, some of the technically most important and most effective inhibitors for use in acid bath or cleaning with acids are toxic and therefore subjected to extensive handling and storage restrictions. Accordingly, the replacement of some toxic expensive chemical inhibitors by green inhibitors (i.e. environmentally friendly inhibitors) obtained from natural sources is required to keep

the environment more healthy, safely and under pollution control. Natural products of plant origin contain different organic compounds (e.g. alkaloids, tannins, pigments organic and amino acids) and most are known to have inhibitive actions [6, 16].

Various natural products, e.g. Toppaco extract [17], aloe extract [18], Mahasudarshana Churna extract [19], Azadirachta Indica leaves extract [20], Natural Honey [21, 22], some Herbs extracts [23], Opuntia extract [24], Camel's Urine [25], juice of Citrus Paradisi [26] and artemisia oil [27], etc. have been reported to be very good inhibitors.

Fenugreek is an annual plant widely cultivated for both medicinal and culinary uses. Fenugreek leaves (see Fig. 1b) are used as herb, while Fenugreek seeds (see Fig. 1a) are used as spice in India, China and Middle East for centuries. Fenugreek has been used for numerous traditional indications [28]:

- ◆ Fenugreek seeds are rich in vitamin E and is one of the earliest spices known to man.
- ◆ Fresh fenugreek leaves are beneficial in the treatment of indigestion, flatulence and a sluggish liver.
- ◆ The dried leaves of the fenugreek is used as a quality flavour for meat, fish and vegetable dishes.
- ◆ An infusion of the leaves is used as a gargle for recurrent mouth ulcers. A gargle made from the seeds is best for ordinary sore throat.
- ◆ Fresh Fenugreek leaves paste applied over the scalp regularly before bath helps hair grow, preserves natural color, keeps hair silky and also cures dandruff.
- ◆ Fenugreek seeds made in gruel, given to nursing mothers increase the flow of milk.
- ◆ Topically, the gelatinous texture of fenugreek seed may have some benefit for soothing skin that is irritated by eczema or other conditions. It has also been applied as a warm poultice to relieve muscle aches and gout pain.

However, numerous animal studies and preliminary trials in humans have found that fenugreek seeds can inhibit cancer of the liver, lower blood cholesterol levels and also have an anti-diabetic effect [29]. So, as commonly eaten food, fenugreek is generally regarded as safe [30].

From the above point of view, the present work aimed to test the inhibitive characteristics of aqueous extract of fenugreek leaves (AEFL) as well as of fenugreek seeds (AEFS) for mild steel corrosion in 2.0 M of HCl and H<sub>2</sub>SO<sub>4</sub> solutions at 30° C by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) measurements.

## **Experimental**

### **1- Mild steel**

The utilized mild steel has the following composition: C= 0.250%, Mn=0.480, Si=0.300, Ni=0.040, Cr=0.060, Mo=0.020, S=0.021, P=0.019 and the rest up to 100% Fe.

### **2- Inhibitor**

The studied inhibitor is of natural plant material with the potential name Fenugreek. The dried leaves and seeds of Fenugreek were obtained from Indian productions.

Stock solution of the inhibitor extracts were prepared by boiling 10 g of dried, grounded fenugreek leaves or seeds in 250 ml of de-ionized water for 1 h. The extracts were kept all night and then filtered, completed to 250 ml by de-ionized water. Both the freshly prepared extract and that aged for two months give almost the same results.

### **3- Solutions**

The aggressive solutions were prepared from analytical grade reagents (HCl and H<sub>2</sub>SO<sub>4</sub>) and de-ionized water. The required concentrations (0.5%, 1.0%, 2.0%, 5.0% and 10.0% v/v) of AEFL and AEFS were prepared by diluting with 2.0 M of HCl and H<sub>2</sub>SO<sub>4</sub> solutions. In all experiments, the temperature of solutions was controlled at 30° C using a water thermostat.

## 2- Electrochemical measurements

Electrochemical testing of inhibitors has the major benefit of short measurements time and giving vital information about the mechanism of inhibition. Confidence in these measurements is gained by replication.

The electrochemical cell is a conventional three-electrode Pyrex glass cell. The mild steel specimen was embedded in Teflon holder using epoxy resin with an exposed area of 0.785 cm<sup>2</sup>. A platinum wire was used as an auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE) coupled to a Luggin capillary whose tip was located between the working electrode and the auxiliary electrode.

Electrochemical measurements were run by using a potentiostat/galvanostat (ACM Gill AC instrument model 655) and a personal computer were used. ACM Gill software was used for EIS and PDP analysis. Prior to each experiment, the working electrode was polished successively with different grade of emery papers, then the polished metal surface was rinsed with de-ionized water, ethanol and finally dipped in the tested solution. After 10 minute of electrode immersion to attain open circuit potential, the electrochemical measurements will be done as follows:

**Firstly**, the EIS measurements were carried out using AC signals of amplitude 10 mV peak-to-peak at the open circuit potential in the frequency range of 10 KHz to 0.5 Hz. The charge transfer resistance ( $R_{ct}$ ) values have been calculated from the difference in the impedance at low and high frequencies as suggested by Trsuru *et al.* [31].

The capacitance of the double layer ( $C_{dl}$ ) values are estimated from the frequency ( $f$ ) at which the imaginary component of the impedance ( $-Z''$ ) is maximum and obtained from the equation:

$$f(-Z''_{\max.}) = \frac{1}{2\pi C_{dl} R_{ct}} \quad (1)$$

The percentage inhibition efficiency ( $IE(\%)$ ) values from EIS measurements were calculated from  $R_{ct}$  data as follows:

$$IE_{R_{ct}}(\%) = \left(1 - \frac{R_{ct}^{-1}}{R_{ct^0}^{-1}}\right) \times 100 \quad (2)$$

where  $R_{ct^0}^{-1}$  and  $R_{ct}^{-1}$  are the reciprocals of charge transfer resistance in absence and presence of inhibitor.

**Secondly**, for each experiment, after impedance spectrum was obtained the potentiodynamic current-potential curves will be recorded immediately by changing the electrode potential automatically from -550 to -350 with scan rate of 1 mV s<sup>-1</sup>. Tafel lines extrapolation method was used for detecting  $i_{corr.}$  and  $E_{corr.}$  values for the studied systems. Because of the presence of a degree of non-linearity in the part of the obtained polarization curves, the corresponding anodic and cathodic Tafel slopes ( $b_a$  and  $b_c$ ) were calculated as a slope of the points after corrosion potential ( $i_{corr.}$ ) by  $\pm 50$  mV using a computer least square analysis. The  $IE(\%)$  values from PDP measurements were calculated as follows:

$$IE_{i_{corr.}} (\%) = (1 - \frac{i_{corr.}}{i_{corr.}^o}) \times 100 \quad (3)$$

where  $i_{corr.}^o$  and  $i_{corr.}$  are the corrosion current densities in absence and presence of inhibitor.

All the electrochemical measurements were performed in stagnant aerated solutions adjusted at 30° C.

## **Results and discussion**

### **1- EIS measurements**

Figure 2 and 3 show the Nyquist plots recorded for mild steel in 2.0 M of HCl and H<sub>2</sub>SO<sub>4</sub>, respectively, in the absence and presence of increasing concentrations of AEFL. Similar plots were obtained for mild steel in both acids in the presence of different concentrations of AEFS and not shown. In general, as impedance diagrams for solutions examined have almost a semicircular appearance, it indicates that the corrosion of steel is mainly controlled by a charge transfer process [32-34].

The systems can be simulated by a simple circuit model of the Randle type (see Fig. 4) which consists of parallel combination of resistor,  $R_{ct}$ , and a capacitor,  $C_{dl}$ , both are in series to resistor,  $R_{sol.}$ . Randle equivalent circuit was successfully applied for some corrosion and corrosion inhibition systems [35-41]. All EIS parameters ( $R_{ct}$ ,  $i_{corr}$  and  $C_{dl}$ ) and the  $IE_{R_{ct}}$  (%) obtained for mild steel corrosion in both acids in absence and presence of different concentrations of both AEFL and AEFS were recorded in Table 1. The results in this table can be illustrated as follows:

- In H<sub>2</sub>SO<sub>4</sub> solutions, an acceleration behavior ( $R_{ct}^{inh.} < R_{ct}^{uninh.}$ ,  $i_{corr}^{inh.} > i_{corr}^{uninh.}$  and  $C_{dl}^{inh.} > C_{dl}^{uninh.}$ ) is observed with the addition of low concentrations of AEFL ( $\leq 1.0$  v/v%).
- In general,  $R_{ct}$  value increases with inhibitor concentration leading to a decrease in  $i_{corr}$  for mild steel in the tested solutions. Double layer capacitance value ( $C_{dl}$ ) decreases as the concentration of both extracts increases which indicates the adsorption of the inhibitor on the metal surface.
- Both extracts inhibit mild steel corrosion in 2.0 M HCl solution more than in H<sub>2</sub>SO<sub>4</sub> solution. While in each acid AEFS inhibits mild steel corrosion more than AEFL.

### **2- PDP measurements**

Figures 5 and 6 show the effect of AEFS on the anodic and cathodic polarization curves for mild steel in 2.0 M of HCl and H<sub>2</sub>SO<sub>4</sub>, respectively. Similar curves were obtained in the case of AEFL in both acids and not shown. It was observed that, in HCl and H<sub>2</sub>SO<sub>4</sub>, both extracts increase also both of the anodic and cathodic overpotentials but its influence on the cathodic side is much less obvious (act predominately as anodic inhibitors). All polarization parameters, that is, corrosion potential ( $E_{corr.}$ ), Tafel slopes ( $b_c$  and  $b_a$ ), corrosion current density ( $i_{corr.}$ ) and the corresponding  $IE_{i_{corr.}}$  (%) values for mild steel corrosion in both acids in absence and presence of different concentrations of both extracts were estimated and listed in Table 2 and the following observation could be drawn:

- The anodic ( $b_a$ ) and cathodic ( $b_c$ ) Tafel slopes are approximately constant suggesting the inhibiting action of both extracts by adsorption at the metal surface according to blocking adsorption mechanism. Hence, both extracts decrease the surface area available for anodic dissolution and cathodic hydrogen evolution reaction without affecting the reaction mechanism.



- The values of  $E_{corr.}$  change somewhat to less negative values with increasing extracts concentration in both acids.
- The obtained  $i_{corr.}$  values have the same trend as that obtained from EIS measurements
- The  $IE_{i_{corr.}}$  (%) values are in good agreement with that obtained from EIS measurements.

### 3- Adsorption isotherm

Assuming that the corrosion inhibition were caused by the adsorption of the extract species on mild steel surface from both acids, the degree of surface coverage,  $\Theta$ , for different concentrations of both AEFL and AEFS in both acids was evaluated from EIS and PDP measurements by applying the ratio  $IE(\%)/100$ . Attempts were made to fit  $\Theta$  values to various adsorption isotherms and by far the best fit was obtained with the Langmuir isotherm [42] for both AEFL and AEFS in HCl solutions and with Temkin [43] isotherm for both extracts in H<sub>2</sub>SO<sub>4</sub> solutions. According to Langmuir and Temkin isotherms,  $\Theta$  is related to inhibitor concentration,  $C_{inh.}$ , via the following Eqs., respectively:

$$C_{inh.}\Theta^{-1} = \frac{1}{K_{e.c.a.}} + C_{inh.} \quad (4)$$

$$\Theta = \frac{1}{(-2a)} \ln K_{e.c.a.} + \frac{1}{(-2a)} \ln C_{inh.} \quad (5)$$

Equations 4 and 5 predict a linear plot between values of  $C_{inh.}\Theta^{-1}$  and  $C_{inh.}$  (see Fig. 7) and between values of  $\Theta$  and  $\ln C_{inh.}$  (see Fig. 8), respectively; where  $K_{e.c.a.}$  is the equilibrium constant of inhibitor adsorption and  $a$  is the Frumkin lateral interaction factor [44], describing the molecular interactions in the adsorbed layer and is a measure for the steepness of the adsorption isotherm. It can have both positive and negative values. The more positive the value of  $a$ , the steeper is the adsorption isotherm. It is well known that the standard free energy of adsorption,  $\Delta G_{ads.}^o$ , is related to the equilibrium constant of adsorption,  $K_{e.c.a.}$ , and  $\Delta G_{ads.}^o$  can be calculated by the following equation:

$$\log K_{e.c.a.} = -\log C_{H_2O} - \frac{\Delta G_{ads.}^o}{2.303RT} \quad (6)$$

where  $C_{H_2O}$  is the concentration of water molecules at metal electrolyte interface.

All adsorption parameters obtained for the adsorption of both AEFL and AEFS on mild steel surface from HCl and H<sub>2</sub>SO<sub>4</sub> at 30°C were recorded in Tables 3 and 4, respectively. Inspection of Table 3 and 4, the following results can be obtained:

- The slopes of Langmuir relation are closed to unity indicating that both AEFL and AEFS were adsorbed on mild steel surface from 2.0 M HCl solutions by forming mono adsorbed layer [45] and there was no interactions among the adsorbed species [46, 47].
- The negative values of  $a$  factor indicates the existence of repulsive forces among the adsorbed species on mild steel in H<sub>2</sub>SO<sub>4</sub> solutions emphasizing the lowest inhibitive properties of both AEFL and AEFS in such solutions.
- The negative values of  $\Delta G_{ads.}^o$  indicate spontaneous interaction of inhibitor species with the corroding mild steel surface [48, 49].

- From  $\Delta G_{ads}^o$  values, both AEFL and AEFS have better performance in HCl solutions than in  $H_2SO_4$ . On the other hand, AEFS is more effective corrosion inhibitor than AEFL in both acids

#### 4- Inhibitor constituents and inhibition mechanism

The active constituents in Fenugreek plant are [28]:

**Alkaloides:** Trimethylamine, Neurin, Trigonelline (N-methyl-pyridinum-3-carboxylate), Choline (trimethyl ethanolamine), Gentianine, Carpaine and Betain

**Amino acids:** Isoleucine; 4-hydroxyisoleucine, histidine, leucine, L-tryptophan, alanine and argenine.

**Saponins:** Graecunins, fenugrin B, fenugreekine and trigofenosides A-G.

**Seroidal saponogens:** Yamogenin, diosgenin, smilagenin, sarsasapogenin, tigogenin, neotigogenin, gitogenin, neogitogenin and yuccagenin.

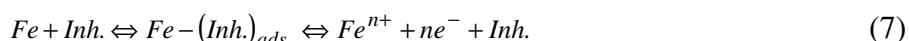
**Fiber:** Gum and neutral detergent.

**Others:** Coumarin, lipids, vitamins and minerals.

Most of the above substances are concentrated in seeds part more than the other parts, explaining why AEFS has good inhibitory action as compared with AEFL. As noticed, fenugreek plant contains a wide variety of N-containing compounds (e.g. amines, amino acids, quaternary N-heterocyclic compounds, etc.). So, the inhibitory action of both AEFL and EEFS can be discussed as follows:

It was reported [50] that N-containing compounds such as amines, amino acids and quaternary ammonium salts are relatively ineffective in prevention corrosion of iron and steel in  $H_2SO_4$  solutions unless certain anions, especially halide (except fluoride) and pseudo-halide ions, are present. This long known synergistic effect [51, 52] is widely used in inhibitor formulation. As a rule of thumb, N-containing compounds exert their best efficiencies in HCl solutions [50].

According to Bockris and Drazic [53], the inhibition mechanism can be explained by the  $Fe-(Inh.)_{ads.}$  intermediates:



This  $Fe-(Inh.)_{ads.}$  intermediate forms an adsorption layer of the inhibitor. The adsorption layer acts as a hindrance to the aggressive solution and enhances the protection of the metal surface. Initially when there is insufficient  $Fe-(Inh.)_{ads.}$  to cover the metal surface, because the inhibitor concentration is low or because the adsorption rate is slow, the metal dissolution takes place at sites on mild steel surface free of  $Fe-(Inh.)_{ads.}$ . If the charge transfer occurs with de-sorption of intermediate complex, the inhibitor will function as an accelerator [54]. With high inhibitor concentration a compact and coherent inhibitor over layer may be formed on mild steel surface, reducing chemical attack of the metal.

An acceleration behavior was reported for mild steel in  $H_2SO_4$  in the presence of some amino phenols and this behavior tends to decrease with the increase in the inhibitor concentration, while they behave very well as corrosion inhibitors in HCl solutions [54]. These observations are similar to that obtained in the present work.

The better performance of both AEFL and AEFS in 2.0 M HCl solutions as compared in  $H_2SO_4$  can be explained in the following way:

In Aqueous acidic solutions amines exist either as neutral molecules or in the form of onium ions while the originally quaternary ammonium ions exist in such solutions only in the cationic form. The possibility of cation adsorption by electrostatic forces is determined by the electric

charge of the electrode with respect to the solution, i.e., by the potential of zero charge (p.z.c.) with respect to  $E_{corr.}$ . This model defines the  $\phi$ -potential [55], which is expressed as:

$$\phi = E_{corr.} - p.z.c. \quad (8)$$

It was reported that the iron (56) and steel (57) surface is positively charged in acid solutions (i.e. positive value for  $\phi$  potential). Accordingly, direct adsorption of onium ions on the positively charged metal surface is not favorable. Accordingly the extent of onium ions adsorption depends on the nature of the anions in acidic solutions. 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 [58]. This results in a change from a positive to a negative charge, thus increasing the electrostatic component of the energy of adsorption [59]. So a close-backed inhibitor film will form on the metal surface and inhibit iron ions to enter the solution. Similarly lesser adsorption of sulphate ions on the metal surface leads to lesser inhibition of corrosion. Antropov [60] suggests that the adsorption of the amine is by means of onium ion. Other authors [61, 62] generally assumed the existence of onium ions in the bulk of the acid solution and subsequent discharge with the formation of molecules at the interface, with the consequent chemisorption through a lone pair of electrons of the hetero-atom. Hackerman and McCafferty [62] suggested that an organic amine-type inhibitor can act in two different ways:

- (1) It can compete with the anions of the acid ( $Cl^-$  or  $SO_4^{2-}$ ) for position on the water-covered metal surface. In doing so the protonated amine loses its protons on entering the double layer and gets chemisorbed by donating a pair of electrons to the metal.
- (2) Protonated amines can be electrostatically adsorbed on the anions-covered metal surface through its hydrogen ions.

Both these mechanisms can increase the inhibitor performance depending on the type of anions in the acidic solution. To elucidate these mechanisms further studies must be done on temperature effect and halide ion additions on the corrosion inhibition of mild steel by AEFL or AEFS in both acids.

### **5- Effect of acid concentration**

The effect of different acid molarities (1 M-5.5 M) on the inhibitive efficiency ( $IE_{R_{ct}}$  (%)) of AEFL and AEFS at concentration level of 2.0 v/v% is shown in Fig. 9. It may be generalized that the inhibition efficiency of both extracts decreases with increase in the concentration of both acids. This behavior may be traced to the increase tendency of the metal to react with acid and liberate hydrogen vigorously [63]. This may not allow the establishment of adsorption process sufficiently and rapidly resulting in decrease of inhibition. However at all the studied acid concentrations the AEFL and AEFS inhibit mild steel corrosion in HCl solutions greater than in  $H_2SO_4$  solutions.

### **Conclusions**

- ◆ In HCl and  $H_2SO_4$  solutions, both AEFL and AEFS act predominately as anodic type inhibitors.
- ◆ The inhibition efficiency of both AEFL and AEFS increases with increasing of their concentration in 2.0 M of both acids, but at certain concentration of both extracts it decreases with increasing concentration of both acids.
- ◆ In HCl solutions, the inhibition efficiency of both AEFL and AEFS was always greater than in  $H_2SO_4$  solutions for otherwise identical conditions.

- ◆ The adsorption of both AEFL and AEFS on mild steel surface in HCl solutions obeys the Langmuir adsorption isotherm, while obeys the Temkin adsorption isotherm in H<sub>2</sub>SO<sub>4</sub> solutions.
- ◆ The obtained results from EIS and PDP measurements are in good agreement.
- ◆ Good correlation between the inhibitor constituents and its inhibition efficiency in both acids was obtained and discussed.

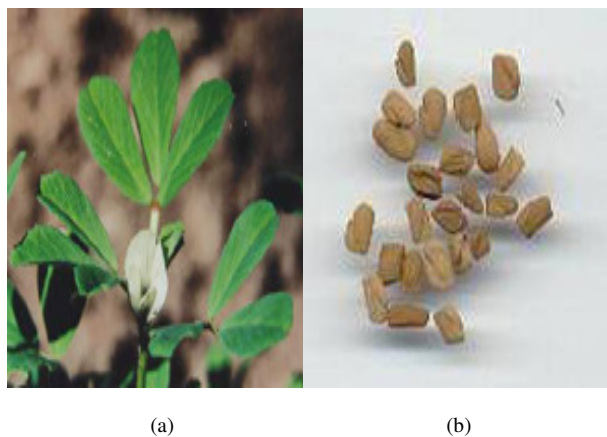
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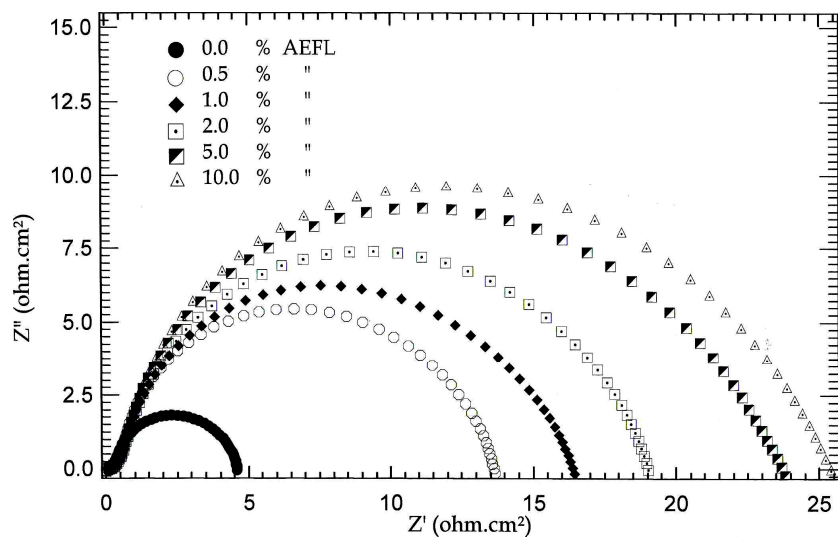


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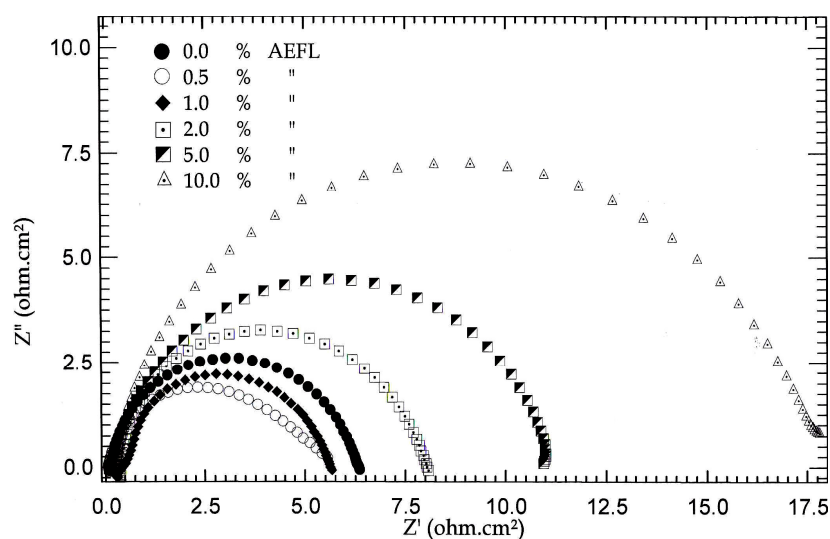
**The Figures:**



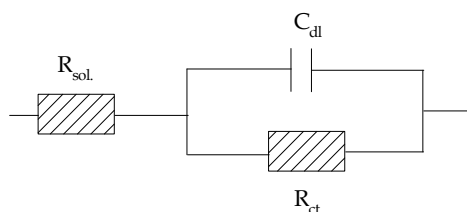
**Fig. 1.** The trifoliate Fenugreek leaves and (b) The yellow rhombic Fenugreek seeds.



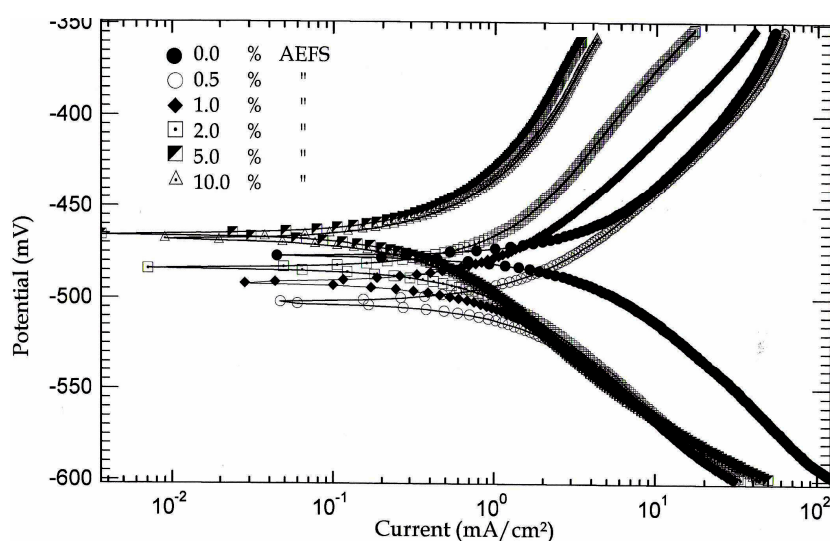
**Fig. 2.** Nyquist plots for mild steel in 2.0 M HCl in absence and presence of different concentrations of AEFL at 30° C.



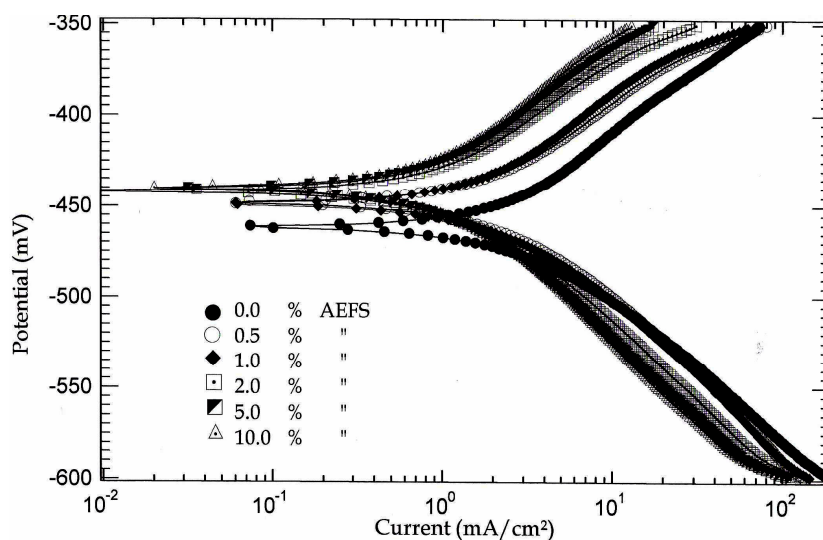
**Fig. 3.** Nyquist plots for mild steel in 2.0 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of different concentrations of AEFL at 30° C.



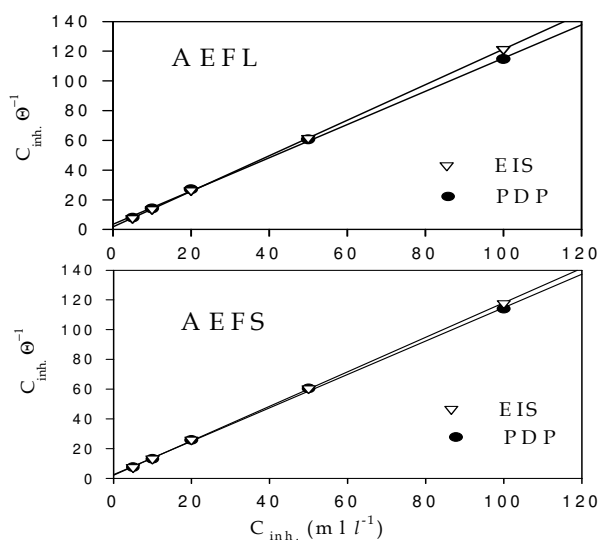
**Fig. 4.** The equivalent circuit model for the metal/solution interface.



**Fig. 5.** Potentiodynamic Polarization curves for mild steel in 2.0 M HCl in absence and presence of different concentrations of AEFS at 30° C.

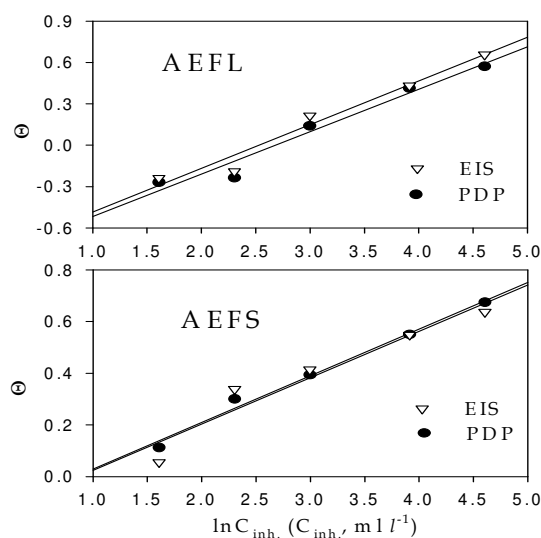


**Fig. 6.** Potentiodynamic Polarization curves for mild steel in 2.0 M  $\text{H}_2\text{SO}_4$  in absence and presence of different concentrations of AEFS at 30° C.

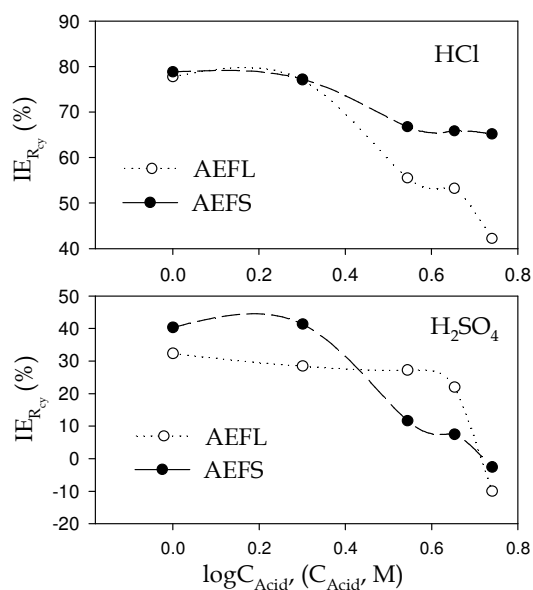


**Fig. 7.** Langmuir isotherm for adsorption of AEFL and AEFS on mild steel surface in 2.0M HCl at 30° C.





**Fig. 8.** Temkin isotherm for adsorption of AEFL and AEFS on mild steel surface in 2.0M  $\text{H}_2\text{SO}_4$  at 30° C.



**Fig. 9.** Effect of acid concentration on inhibition efficiency of 2.0 v/v% AEFL and AEFS for mild steel at 30° C.

## The Tables:

**Table. 1.** EIS parameters and corresponding  $IE_{R_{ct}}$  (%) for mild steel corrosion in 2.0 M of HCl and H<sub>2</sub>SO<sub>4</sub> in absence and presence of different concentrations of AEFL and AEFS.

$C_{inh}$ (v/v %)	HCl				H <sub>2</sub> SO <sub>4</sub>			
	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> )	$C_{dl}$ ( $\mu$ F cm <sup>-2</sup> )	$I_{corr}$ (mA cm <sup>-2</sup> )	IE (%)	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> )	$C_{dl}$ ( $\mu$ F cm <sup>-2</sup> )	$I_{corr}$ (mA cm <sup>-2</sup> )	IE (%)
AEFL								
0.0	4.33	1883.0	6.03	-	6.06	1706.0	4.19	-
0.5	13.41	745.5	1.95	67.71	4.90	7264.0	5.33	-23.67
1.0	16.23	737.8	1.61	73.32	5.09	2949.0	5.13	-19.06
2.0	18.84	657.1	1.39	77.02	7.73	1568.0	3.37	21.60
5.0	23.08	515.6	1.13	81.24	10.68	1028.0	2.44	43.26
10.0	24.56	487.8	1.06	82.37	17.71	546.1	1.47	65.78
AEFS								
0.5	13.47	741.6	1.94	67.85	6.41	1876.0	4.06	5.46
1.0	18.07	725.8	1.44	76.04	9.15	1704.0	2.85	33.77
2.0	18.98	623.3	1.37	77.19	10.33	979.0	2.53	41.34
5.0	24.92	439.5	1.05	82.62	13.41	827.6	1.95	54.81
10.0	28.61	372.9	0.91	84.87	16.68	667.9	1.56	63.67

**Table. 2.** PDP parameters and corresponding  $IE_{i_{corr}}$  (%) for mild steel corrosion in 2.0 M of HCl and H<sub>2</sub>SO<sub>4</sub> in absence and presence of different concentrations of AEFL and AEFS.

$C_{inh}$ (v/v %)	HCl					H <sub>2</sub> SO <sub>4</sub>				
	$-E_{corr}$ (mV)	$-b_c$ (mV)	$b_a$ (mV)	$I_{corr}$ (mA cm <sup>-2</sup> )	IE (%)	$-E_{corr}$ (mV)	$-b_c$ (mV)	$b_a$ (mV)	$I_{corr}$ (mA cm <sup>-2</sup> )	IE (%)
AEFL										
0.0	478	65	73	6.04	-	462	51	60	4.30	-
0.5	480	64	70	2.82	53.31	450	47	55	5.46	-26.98
1.0	467	61	71	1.76	70.86	443	46	52	5.32	-23.72
2.0	467	63	74	1.57	74.01	439	45	51	3.70	13.95
5.0	466	64	73	1.06	82.45	437	47	47	2.52	41.40
10.0	465	65	70	0.77	87.25	437	45	47	1.84	57.21
AEFS										
0.0	478	65	73	6.04	-	462	51	60	4.30	-
0.5	503	61	71	1.92	68.21	450	42	53	3.82	11.16
1.0	490	65	73	1.36	77.48	448	43	46	3.01	30.00
2.0	485	51	65	1.33	77.98	442	43	49	2.61	39.30
5.0	466	56	65	1.03	82.95	441	41	46	1.94	54.88
10.0	468	58	62	0.74	87.75	439	39	44	1.40	67.44

**Table. 3.** Langmuir adsorption isotherm parameters for AEFL and AEFS onto mild steel in HCl at 30° C.

$C_{inh.}$ v/v %	Adsorption parameters					
	Slope		$K_{e.c.a.} (ml^{-1} l)$		$\Delta G_{ads}^o$ KJ mol <sup>-1</sup>	
	EIS	PDP	EIS	PDP	EIS	PDP
AEFL	1.20	1.12	0.506	0.290	-15.69	-14.29
AEFS	1.20	1.12	0.526	0.408	-15.79	-15.15

**Table. 4.** Temkin adsorption isotherm parameters for AEFL and AEFS onto mild steel in H<sub>2</sub>SO<sub>4</sub> at 30° C.

$C_{inh.}$ v/v %	Adsorption parameters					
	a		$K_{e.c.a.} (ml^{-1} l)$		$\Delta G_{ads}^o$ KJ mol <sup>-1</sup>	
	EIS	PDP	EIS	PDP	EIS	PDP
AEFL	-1.58	-1.62	0.080	0.068	-11.04	-10.62
AEFS	-2.79	-2.78	0.421	0.389	-15.23	-15.03