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Comparative Study on the Corrosion Inhibition of Mild Steel by Aqueous Extract of Fenugreek Seeds and Leaves 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 sin HCl and H_2SO_4 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_2SO_4 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_2SO_4 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.

Key words: Corrosion inhibition, aqueous extract, acidic solutions, AEFL, AEFS

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 for steel in acidic solutions, e.g. isothioronium iodides (Arab and Noor, 1992, 1993), quaternary ammonium salts of N-containing heterocyclics (Noor and Moubaraki, 2003; Noor, 2005), bipyrazolic derivatives (Tebbji *et al*., 2005), thiadiazoles derivatives (Lebrini *et al*., 2005), isoxazolidines (Ali *et al*., 2005) and azoles (Popova, 2007). 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.

Accordingly, the replacement of some toxic expensive chemical inhibitors by inhibitors obtained from natural sources is required to keep the environment more healthy, safely and under pollution control. Various natural products, e.g. Artemisia oil (Bouyanzer and Hammouti, 2004), Lawsonia extract (El-Etre *et al*., 2005), Telfaria occidentalis extract (Oguzie, 2005), Ammi majus L. fruit extracts (Arab *et al*., 2005), juice of Prunus cerasus (Ashassi-Sorkhabi and Seifzadeh, 2006), Pennyroyal oil from Mentha oulegium (Bouyanzer *et al*., 2006), Occimum viridis extract (Oguzie, 2006) etc. have been reported to be good inhibitors for steel in acidic solutions.

Fenugreek is an annual plant (Fig. 1) widely cultivated for both medicinal and culinary uses. Several human intervention trials demonstrated that the antidiabetic effects of fenugreek seeds ameliorate most metabolic symptoms associated with type-1 and type-2 diabetes in both animals and humens models (Ribes *et al*., 1986; Srinivas, 2005). In recent research, fenugreek seeds were experimentally shown to protect against cancers of

Fig. 1: The trifoliate fenugreek leaves and (b) the yellow rhombic fenugreek seed

the breast. So, as commonly eaten food, fenugreek is generally regarded as safe.

From the above point of view, the present work aimed to give comparative study by testing the Aqueous Extract of Fenugreek Leaves (AEFL) and Fenugreek Seeds (AEFS) as natural inhibitors for mild steel corrosion in 2.0 M solution of HCl and H_2SO_4 at 30° C by using Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization (PDP) measurements.

MATERIALS AND METHODS

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.

Preparation of Fenugreek extracts: The dried leaves and seeds of Fenugreek were obtained from Indian productions. Stock solution of the inhibitor extract were prepared by boiling 10 g of dried, grounded fenugreek seeds or leaves in 250 mL of de-ionized water for 1 h. The extract was left all night and then filtered and completed to 250 mL by de-ionized water. Both the freshly prepared extract and that aged in a refrigerator for tow months give almost the same results.

Solutions: The aggressive solutions were prepared from analytical grade reagents (HCl and H_2SO_4) 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_2SO_4 solutions. In all experiments, the temperature of solutions was controlled at 30°C using a water thermostat.

Electrochemical measurements: Electrochemical testing of inhibitors has the major benefit of short measurements time and giving vital information about the mechanism of inhibition. 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^2. 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 potentiostate/galvanoatate (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 min 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. 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:

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

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

$$IE_{R_{ct}}(\%) = (1 - \frac{R_{ct}^{-1}}{R_{ct^{o}}^{-1}}) \times 100 \qquad (2)$$

Where, $R_{ct^{o}}^{-1}$ 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^{-1}. 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 ±50 mV using a computer least square analysis. The IE (%) values from PDP measurements were calculated as follows:

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

Where, i^{o}_{corr} 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

EIS measurements: Figure 2 and 3 show the Nyquist plots recorded for mild steel in 2.0 M of HCl and H_2SO_4, 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 (Metikoš-Huković and Babic, 1998; Larabi and Harek, 2004; Bentiss *et al*., 2005).

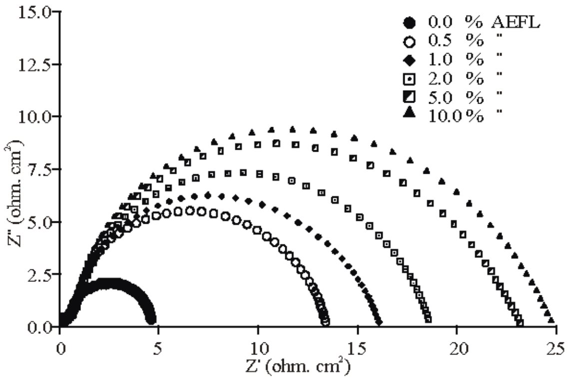

Fig. 2: Nyquist plots for mild steel in 2.0 M HCl in absence and presence of different concentrations of AEFL at 30°C

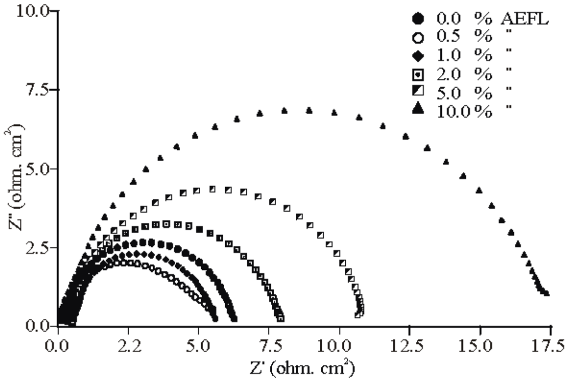

Fig. 3: Nyquist plots for mild steel in 2.0 M H_2SO_4 in absence and presence of different concentrations of AEFL at 30°C

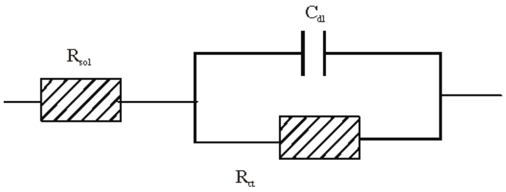

Fig. 4: The equivalent circuit model for the metal/solution interface

Table 1: EIS parameters and corresponding IE_{Rct} (%) for mild steel corrosion in 2.0 M of HCl and H_2SO_4 in absence and presence of different concentrations of AEFL and AEFS

	HC1			H_2SO_4		
C_{inh} (v/v %)	R_{ct} (Ω cm²)	$C_{dl;}$ (μF cm⁻²)	IE (%)	R_{ct} (Ω cm²)	$C_{dl;}$ (μF cm⁻²)	IE (%)
AEFL						
0.0	4.33	1883.0	-	6.06	1706.0	-
0.5	13.41	745.5	67.71	4.90	7264.0	-23.67
1.0	16.23	737.8	73.32	5.09	2949.0	-19.06
2.0	18.84	657.1	77.02	7.73	1568.0	21.60
5.0	23.08	515.6	81.24	10.68	1028.0	43.26
10.0	24.56	487.8	82.37	17.71	546.1	65.78
AEFS						
0.5	13.47	741.6	67.85	6.41	1876.0	5.46
1.0	18.07	725.8	76.04	9.15	1704.0	33.77
2.0	18.98	623.3	77.19	10.33	979.0	41.34
5.0	24.92	439.5	82.62	13.41	827.6	54.81
10.0	28.61	372.9	84.87	16.68	667.9	63.67

The impedance systems can be simulated by a simple circuit model of Randle type (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 (Zhao *et al*., 2005; Dehri and Ozcan, 2006; Khaled, 2006). All the obtained EIS parameters (R_{ct} and C_{dlt}) and the IE_{Rct} for mild steel corrosion in both acids in absence and presence of different concentrations of AEFL and AEFS were recorded in Table 1. The results in this table can be illustrated as follows:

- In H_2SO_4 solutions, an acceleration behavior ($R_{ct}^{inh.} < R_{ct}^{uninh.}$ and $C_{dl}^{inh.} > C_{dl}^{uninh.}$) is observed with the addition of low concentrations of AEFL (0.5 and 1.0 v/v%.).
- In general, R_{ct} value increases and C_{dl} value decreases as the concentration of both extracts increases in both acids 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_2SO_4 solution. While in each acid AEFS inhibits mild steel corrosion more than AEFL.

PDP measurements: Figure 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_2SO_4, respectively. Similar curves were obtained in the case of AEFL in both acids and not shown. It was observed that, in HCl and H_2SO_4, both extracts increase also both of the anodic and cathodic overpotentials but its influence on the cathodic side is much less obvious (i.e. 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 $IE_{icorr.}$ (%) 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:

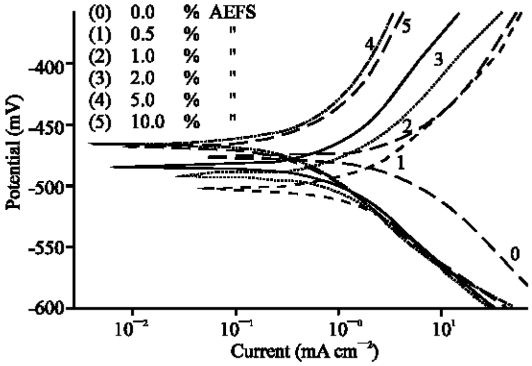

Fig. 5: The equivalent circuit model for the metal/ solution interface

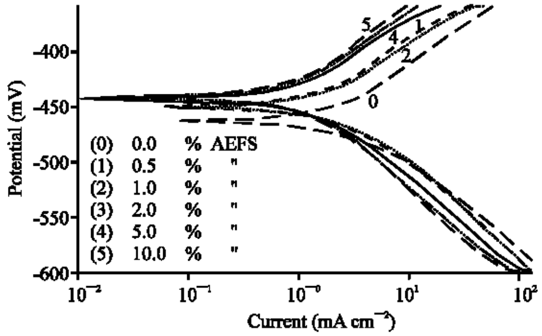

Fig. 6: Potentiodynamic polarization curves for mild steel in 2.0 M HCl in absence and presence of different concentrations of AEFS at 30°C

- The anodic (b_c) and cathodic (b_a) Tafel slopes do not change significantly in inhibited solution as compared to uninhibited solution. This observations suggest that both AEFL and AEFS adsorb on the metal surface by blocking the active sites of steel surface without affecting the mechanism of corrosion. This type of behaviour has been observed for mild steel in acid solutions containing Ammi majus L. fruit extracts (Arab *et al.*, 2005).
- The values of $E_{corr.}$ change somewhat to less negative values with increasing extracts concentration in both acids.
- The $IE_{icorr.}$ values are in good agreement with that obtained from EIS measurements.

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, Θ, 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 Θ values to various adsorption isotherms and by far the best fit was obtained with the Langmuir isotherm (1917) for both AEFL and AEFS in HCl solutions and with Temkin (1941) isotherm for both extracts in H_2SO_4 solutions. According to Langmuir and Temkin isotherms,Θ is related to inhibitor concentration, C_{inh}, via the following equations, respectively:

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

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

Equation 4 and 5 predict a linear plot between values of $C_{inh.}\Theta^{-1}$ and $C_{inh.}$ (Fig. 7) and between values of Θ and $C_{inh.}$(Fig. 8), respectively; where $K_{ads.}$ is the equilibrium constant of inhibitor adsorption and a is the Frumkin lateral interaction factor (Drazic *et al.*, 1994), 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, ΔG°_{ads}, is related to the equilibrium constant of adsorption, K_{ads} and ΔG°_{ads} can be calculated by the following equation:

$$\log K_{ads.} = -\log C_{H_2O} - \frac{\Delta G^{\circ}_{ads.}}{2.303RT} \tag{6}$$

Table 2: PDP parameters and corresponding $IE_{icorr.}$ for mild steel corrosion in 2.0 M of HCl and H_2SO_4 in absence and presence of different concentrations of AEFL and AEFS

	Hcl					H_2SO_4				
C_{inh} (v/v %)	$-E_{corr}$ (mV)	$-b_c$ (mV)	b_a (mV)	I_{corr} (mA cm^{-2})	IE (%)	$-E_{corr}$ (mV)	$-b_c$ (mV)	b_a (mV)	I_{corr} (mA cm^{-2})	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

	Adsorption parameters					
	Slope		$K_{e.c.a}$ (mL^{-1} L)		$\Delta G^{o}_{ads.}$ KJ mol^{-1}	
$C_{inh.}$ v/v %	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_2SO_4 at 30° C

	Adsorption parameters					
	a		$K_{e.c.a.}$ (mL^{-1} L)		$\Delta G^{o}_{ads.}$ KJ mol^{-1}	
$C_{inh.}$ v/v %	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

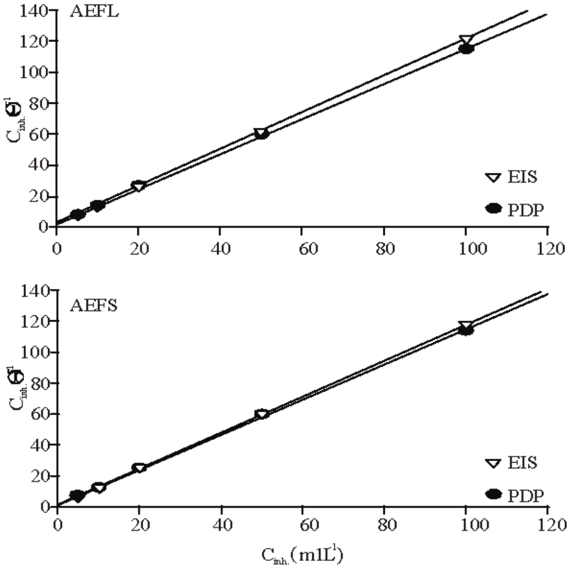

Fig. 7: Langmuir isotherm for adsorption of AEFL and AEFS on mild steel surface in 2.0M HCl at 30°C

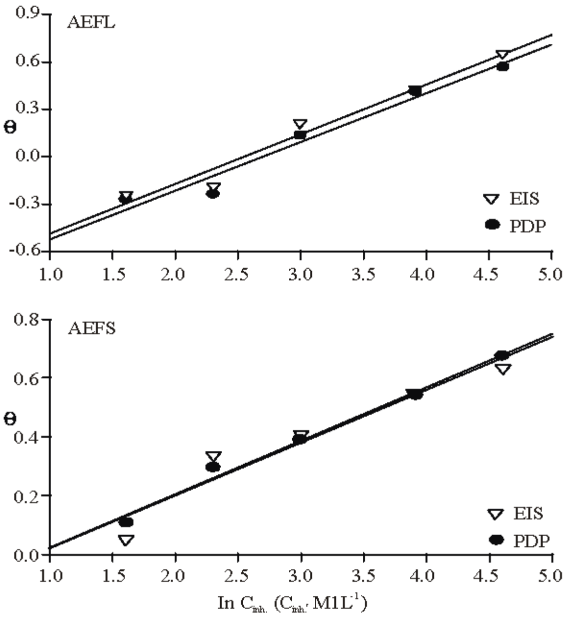

Fig. 8: Temkin isotherm for adsorption of AEFL and AEFS on mild steel surface in 2.0M H_2SO_4 at 30°C

Where, C_{H_2O} is the concentration of water molecules at metal electrolyte interface in mL L^{-1}.

All adsorption parameters obtained for the adsorption of both AEFL and AEFS on mild steel surface from HCl and H_2SO_4 at 30°C were recorded in Table 3 and 4, respectively. Inspection of Table 3 and 4, the following results can be obtained:

- The negative values of a factor indicates the existence of repulsive forces among the adsorbed species on mild steel from H_2SO_4 solutions emphasizing the lower inhibitive properties of both AEFL and AEFS in such solutions as compared to that detected in HCl solutions.

- The negative values of ΔG^{o}_{ads} indicate spontaneous interaction of inhibitor species with the corroding mild steel surface.
- From ΔG^{o}_{ads} 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.

Inhibitor constituents and inhibition mechanism: The active constituents in Fenugreek plant are (http://www.fenugreek-seeds.com/).

Alkaloides: Trime thylamine, 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 trigofoenosides A-G.

Seroidal sapinogens: 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 (http://www.swsbm.com/Constituents/constituentsQ-Z.html), 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 ammonium of N-heterocyclic compounds, etc.) which may play an important role in interpretation the obtained results. It was reported (Schmitt, 1984) that as a rule of thumb, N-containing compounds such as amines, amino acids and quaternary ammonium salts exert their best efficiencies in prevention corrosion of iron and steel in HCl solutions while they are relatively ineffective in H_2SO_4 and this behaviour is in good agreement with the obtained results in the present research.

As known, in aqueous acidic solutions amines exist either as neutral molecules or in the form of onium ions. 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 (PZC) with respect to $E_{corr.}$. This model defines the ϕ-potential (Banerjee and Malhotra, 1992), which is expressed as:

$$\phi = E_{corr.} - p.z.c. \tag{8}$$

There are some evidence (Banerjee and Malhotra, 1992; Lebrini *et al.*, 2005) revealed that mild steel surface is positively charged in acid solutions (i.e. positive value for ϕ potential). So, 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 (Muralidharan *et al.*, 1994). This results in a change from a positive to a negative charge, thus increasing the electrostatic component of the energy of adsorption. 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 and in some cases of low inhibitor concentration may lead to accelerate corrosion rate. 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 (Rengamani *et al.*, 1994). These observations are similar to that obtained in the present research.

Moreover, it was reported (Muralidharan *et al.*, 1994) that organic amine-type inhibitors can act in acidic solutions in two different ways:

- 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.
- 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 such as studying the effect of temperature and halide ion addition on the performance of fenugreek extract.

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

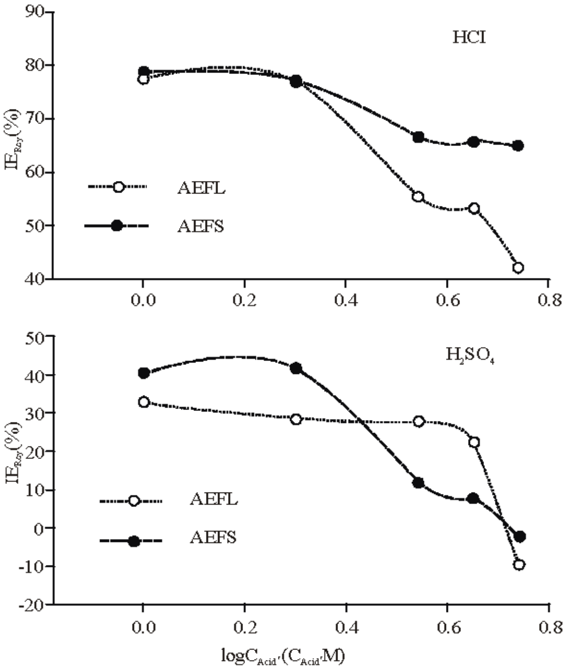

Fig. 9: Effect of acid concentration on inhibition efficiency of 2.0 v/v% AEFL and AEFS for mild steel at 30°C

2.0 v/v% is shown in Fig. 9. It may be generalized that the inhibition efficiency of both extracts decreases with increasing the concentration of both acids and this behaviour is more pronounced in the case of H_2SO_4 solutions. This behavior may be traced to the increase tendency of the metal to react with acid and liberate hydrogen vigorously (Talati and Gandhi, 1983). 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.

CONCLUSION

- 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_2SO_4 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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