RESULTS AND DISCUSSION

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The present study entitled "***Adsorption and Inhibitive properties of extracts of Leaf sheath and Staminate flower of Cocos Nucifera as green inhibitors for mild steel in HCl medium***" deals with the assessment of corrosion inhibition efficiency of some plant materials-*leaf sheath and staminate flower* of coconut tree for mild steel in 1M HCl under static conditions. The inhibitive action as anticipated depended on the concentration of the inhibitor, period of immersion and the temperature of the attacking acid. Corrosion rate and inhibition efficiency were calculated using

- Weight loss measurement
- Polarization measurement

Weight loss measurement

Evaluation of leaf sheath extract of Cocos Nucifera as an inhibitor

The acid extract of leaf sheath in 1M HCl has been tried for its potency in the retardation of corrosion of mild steel. It has been evaluated using the following parameters by weight loss method

- Concentration of the inhibitor
- Immersion time and
- Temperature

Effect of concentration of the inhibitor

The concentration of the inhibitor plays an important role to fix an effective concentration for the extract under study. The effect of inhibitor on the dissolution of mild steel in 1M HCl media has been investigated by conducting the tests with various concentration of the extract (0.05% - 0.45% i.e., 1ml to 9ml of 5% extract). The results are illustrated in the table (1) and fig (1&2). The data showed that the corrosion rate of mild steel decreased with increase in concentration. The corrosion rate decreased with 0.05% to 0.3% of the extract. From the data the maximum enhancement of inhibition is noted with 0.3% of the extract. It was considered as an optimum concentration. 94.9% was noted to be maximum inhibition efficiency at 0.3% concentration. Maximum inhibition efficiency with increase in concentration of the extract may be attributed to the increase in the surface coverage of the inhibitor molecule on the mild steel surface due to adsorption.

Impact of immersion time

To determine the effect of immersion period on inhibitive efficiency, weight losses were determined in 1M HCl for immersion periods of ½, 1, 3,6,12 and 24hrs.

The variation of weight loss with exposure time for the mild steel specimen immersed in 1M HCl with and without the addition of varied concentration of leaf sheath extract are presented in the table(1) and fig(1). From the experimental results it can be concluded that the inhibitor molecule are being adsorbed on the mild steel surface effectively up to 6hrs and after that there is slight decrease in inhibition efficiency up to 12 hrs and then there is increase in inhibition efficiency after 12 hrs. In the present investigation it is also observed that the inhibitor functions very well at higher concentration for all periods of immersion (maximum inhibition efficiency 94.9% at 0.3%). Hence it is suggested that higher concentration of the inhibitor might be used in the pickling bath. The increase of inhibition efficiency with respect to time of immersion indicates the stability of adsorbed layer on the metal surface.

Effect of temperature

Temperature can modify the interaction between the mild steel surface and the acid in the absence and presence of inhibitor.

Temperature studies were carried out in the absence and presence of varying concentration of the inhibitor at 303K, 315K, 325K, 335K, and 345K. The results are presented in figure (3& 4) and table (2). Inhibition efficiency increased with increase in temperature up to 335K, with higher concentrations of the inhibitor. Further increase in temperature showed a decrease in efficiency. The decreased protection efficiency at high temperature may be explained from the fact that increase of temperature affected the rate of adsorption / desorption ratio and if the rate of desorption was faster than the rate of adsorption, there might be decrease in inhibition efficiency with temperature [G. L. Zacchini et al., 1971].

Fig-1

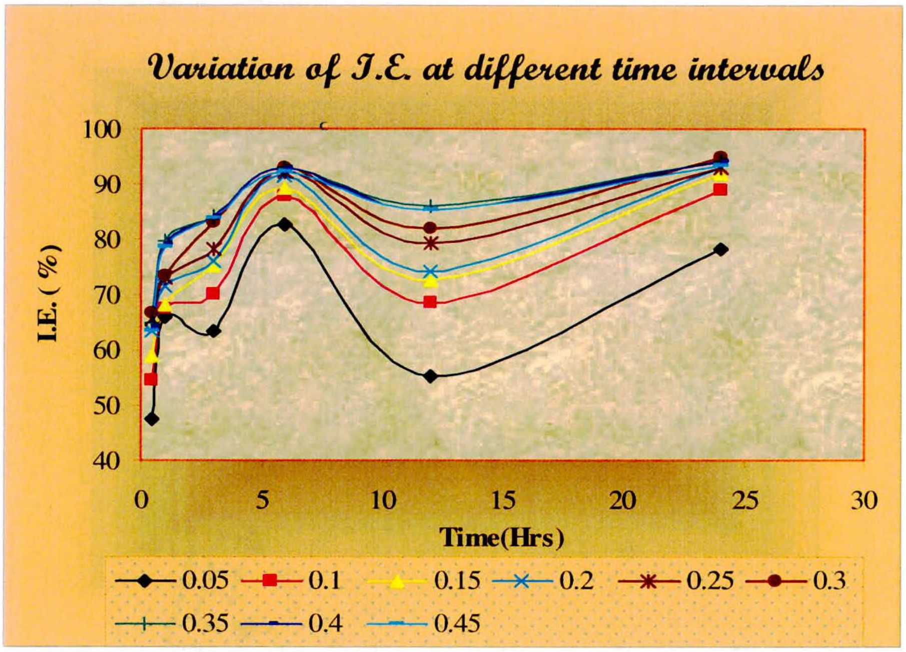

Variation of I.E. at different time intervals
I.E. (%)
100
90
80
70
60
50
40
0
5
10
15
20
25
30
Time(Hrs)
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45

Fig-2

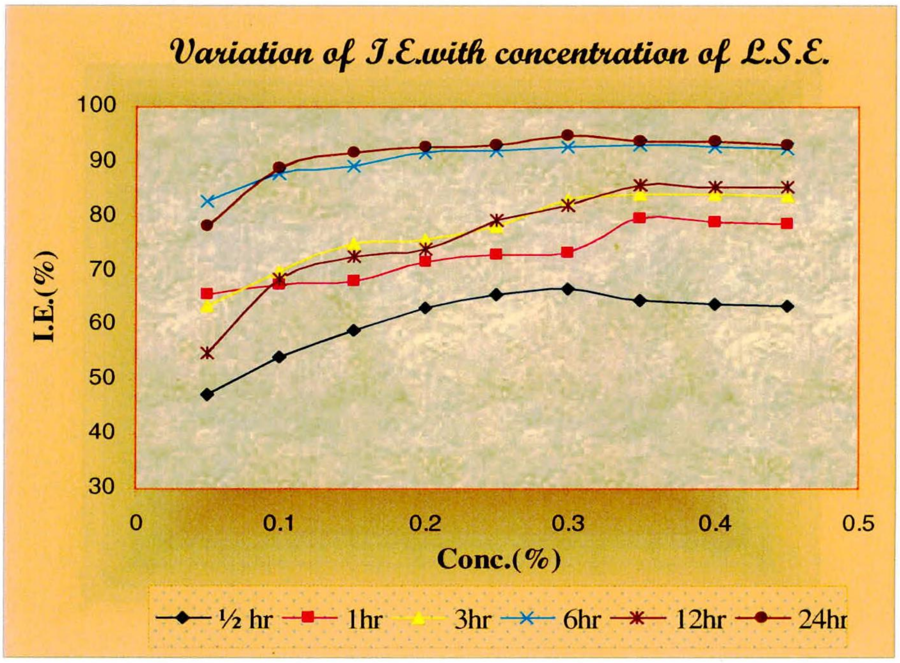

Variation of I.E.with concentration of L.S.E.
I.E.(%)
100
90
80
70
60
50
40
30
0
0.1
0.2
0.3
0.4
0.5
Conc.(%)
½ hr
1hr
3hr
6hr
12hr
24hr

Table-1

Variation of IE of L.S.E. with concentration and time of immersion in HCl

Conc. (%)	Immersion Time(Hrs)											
	½		1		3		6		12		24	
	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)
Blank	524	-	73	-	583	-	839	-	240	-	728	-
0.05	275	47.4	25	65.8	212	63.5	144	82.7	107	55.1	158	78.2
1	238	54.4	23	67.5	175	69.9	101	87.8	75	68.6	79	89.0
0.15	214	59.0	23	68.1	144	75.2	90	89.2	65	72.5	59	91.8
0.2	192	63.2	20	71.6	140	75.9	70	91.6	62	74.0	52	92.8
0.25	179	65.7	19	72.8	127	78.2	65	92.2	49	79.3	50	93.0
0.3	173	66.8	19	73.2	99	82.9	60	92.8	43	82.0	36	94.9
0.35	184	64.7	14	79.5	91	84.2	57	93.1	33	85.9	44	93.9
0.4	188	64.0	15	78.8	93	83.9	60	92.8	35	85.3	44	93.9
0.45	191	63.5	15	78.4	95	83.6	63	92.4	35	85.3	49	93.2

Fig-3

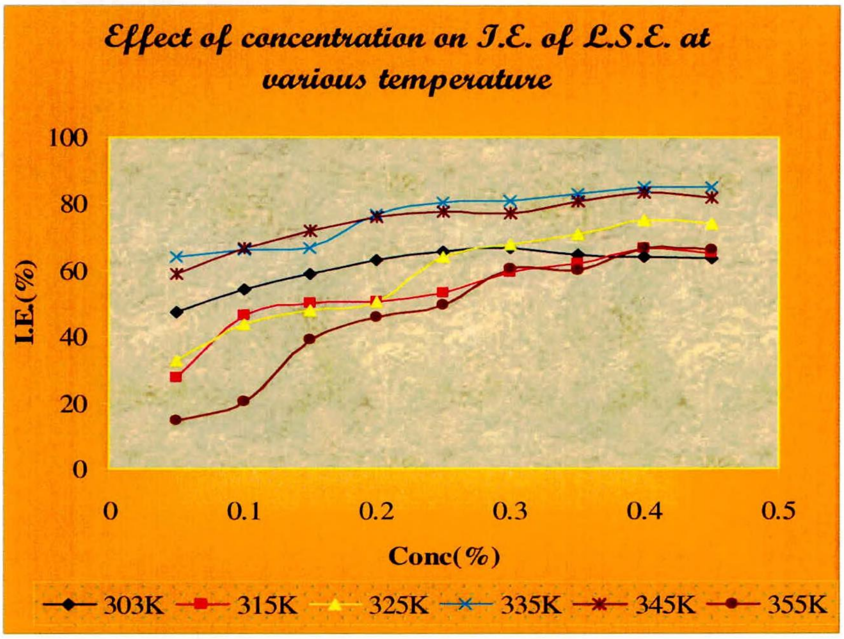

Effect of concentration on I.E. of L.S.E. at various temperature
100
80
60
40
20
0
I.E.(%)
0
0.1
0.2
0.3
0.4
0.5
Conc(%)
303K
315K
325K
335K
345K
355K

Fig-4

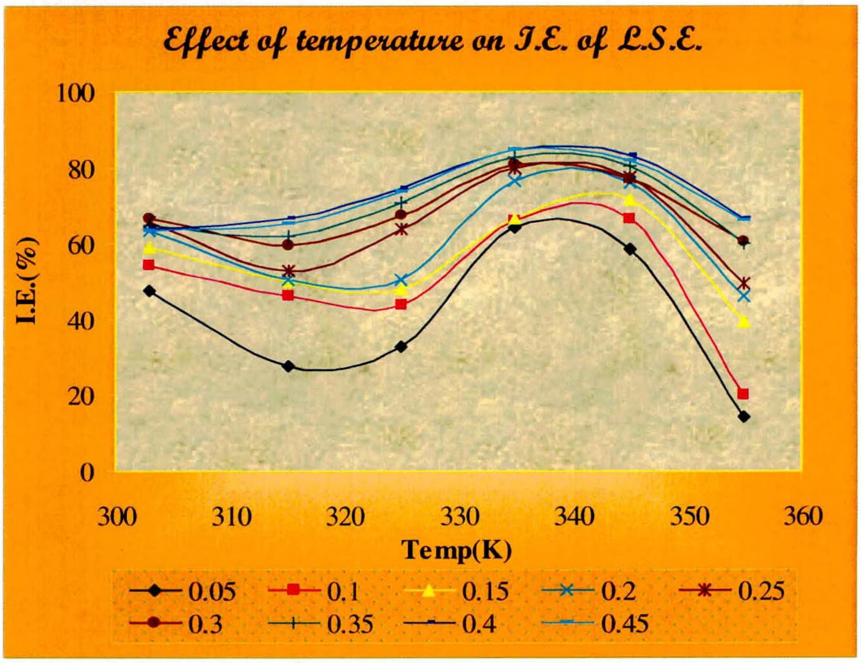

Effect of temperature on I.E. of L.S.E.
100
80
60
40
20
0
I.E.(%)
300
310
320
330
340
350
360
Temp(K)
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45

Table-2

Influence of temperature on corrosion rate and inhibition efficiency of L.S.E

Conc. (%)	Temperature(K)											
	303		315		325		335		345		355	
	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)
Blank	524	-	977	-	2032	-	9939	-	19899	-	16869	-
0.05	275	47.4	707	27.6	1362	32.9	3550	64.2	8184	58.8	14431	14.4
1	238	54.4	524	46.3	1145	43.6	3372	66.0	6631	66.6	13457	20.2
0.15	214	59.0	489	49.9	1055	48.0	3302	66.7	5537	72.1	10232	39.3
0.2	192	63.2	485	50.3	1009	50.3	2333	76.5	4773	76.0	9103	46.0
0.25	179	65.7	459	52.9	730	64.0	1959	80.2	4483	77.4	8473	49.7
0.3	173	66.8	395	59.5	653	67.8	1899	80.8	4565	77.0	6675	60.4
0.35	184	64.7	320	61.8	590	70.9	1698	82.9	3829	80.7	6717	60.1
0.4	188	64.0	327	66.5	509	74.9	1488	85.0	3285	83.4	5609	66.7
0.45	191	63.5	338	65.3	527	74.0	1517	84.7	3580	82.0	5710	66.1

Effect of staminate flower extract of Cocos Nucifera on the dissolution of mild steel in 1M HCl

The effect of staminate flower extract on the free dissolution of mild steel in 1M HCl has been evaluated using the following parameters

- Concentration of the inhibitor
- Immersion time and
- Temperature

Effect of concentration of the inhibitor

The elucidation of the effectiveness of the inhibitor in the acidic medium with respect to the concentration of the inhibitor has been carried out by varying the dosage range of the extract from 0.05% to 0.45% and the results obtained are tabulated in table(3).

The figure (5) represents the variation of inhibition efficiency with extract concentration. From the figure it is imperative that the efficiency of the inhibitor was found to increase with increase in concentration of the extract and reaches a maximum value of 97.3% at 0.3% concentration for various immersion periods. Increase in inhibition effect with increase in concentration of the extract inferred that there is an increase in surface area of the adsorbed molecules of the extract resulting in decrease in dissolution of mild steel.

Effect of immersion time

An effort has been taken to find out the optimum time of immersion for the extract under investigation and the results are tabulated in table (3). Effect of time of immersion on inhibition efficiency is pictorially represented in the figure (6). Inspection of the table reveals that the inhibition efficiency of S.F.E was 79.1% at ½ an hr and 64.2% in 1hr at higher concentration. This may be due to the lesser adsorption at ½ hr and 1hr after that as the period of immersion increases the adsorbed molecules on the surface increases and it was found to be 97.3% at 0.3% concentration.

From the experimental results it was found that the S.F.E. works out very well at 3, 6, 12 and 24 hrs duration.

Table-3

Influence of concentration of S.F.E. and time on the inhibition efficiency and corrosion rate of MS

Conc. (%)	Immersion Time(Hrs)											
	½		1		3		6		12		24	
	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)
Blank	**893**	**-**	**36**	**-**	**1006**	**-**	**377**	**-**	**1531**	**-**	**1606**	**-**
0.05	**307**	**65.6**	**19**	**46.5**	**96**	**90.3**	**61**	**83.7**	**171**	**88.7**	**74**	**95.3**
1	**256**	**71.3**	**16**	**55.4**	**87**	**91.3**	**60**	**84.1**	**152**	**90.0**	**70**	**95.6**
0.15	**241**	**72.9**	**15**	**57.5**	**87**	**91.2**	**59**	**84.3**	**115**	**92.4**	**52**	**96.7**
0.2	**220**	**75.3**	**13**	**62.3**	**76**	**92.4**	**55**	**85.2**	**75**	**95.0**	**49**	**96.9**
0.25	**196**	**78.0**	**13**	**63.2**	**69**	**93.0**	**55**	**85.2**	**58**	**96.2**	**44**	**97.2**
0.3	**186**	**79.1**	**12**	**64.2**	**66**	**93.4**	**48**	**87.0**	**52**	**96.6**	**42**	**97.3**
0.35	**192**	**78.4**	**12**	**66.1**	**59**	**94.1**	**51**	**86.4**	**53**	**96.5**	**47**	**97.0**
0.4	**192**	**78.4**	**12**	**64.8**	**64**	**93.5**	**52**	**86.2**	**68**	**95.5**	**44**	**97.2**
0.45	**195**	**78.1**	**12**	**64.8**	**65**	**93.5**	**56**	**85.1**	**70**	**95.3**	**44**	**97.2**

Fig-5

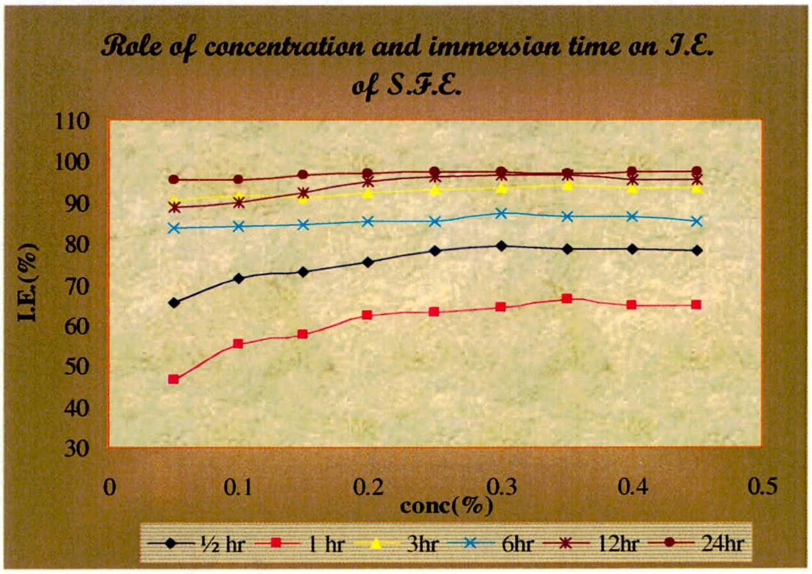
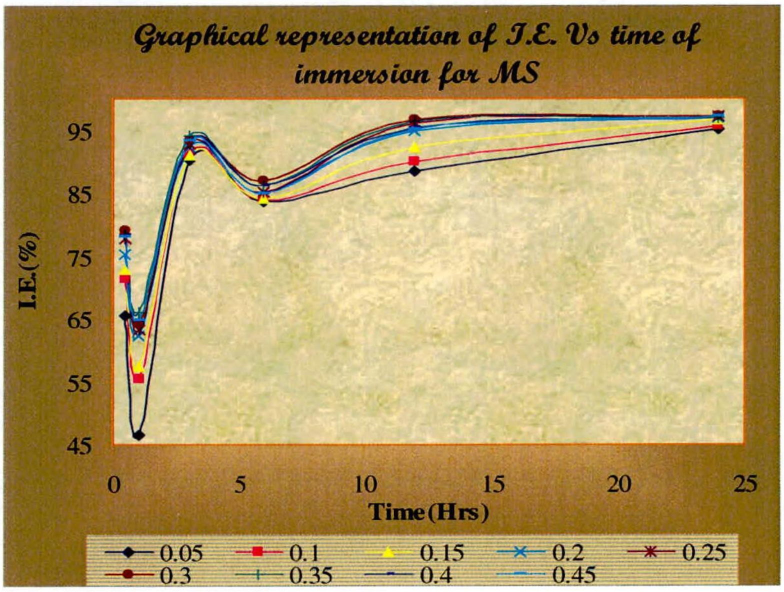


Fig-6



Effect of temperature

To calculate the kinetic and thermodynamic parameters of corrosion, the effect of temperature on the corrosion behaviour of mild steel in 1M HCl has been studied. Table (4) shows the relationship between temperature and the inhibitor efficiency.

The maximum efficiency was observed as 90.9% at 345K. With rise in temperature the efficiency was found to decrease.

According to Rashmi Arrora and R. S. Chaudhary (NCCI 2002) the above observation can be explained as adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between these two processes at a particular temperature. With the increase of temperature of equilibrium between adsorption and desorption processes is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperature especially at low concentration of the inhibitor.

Fig-7

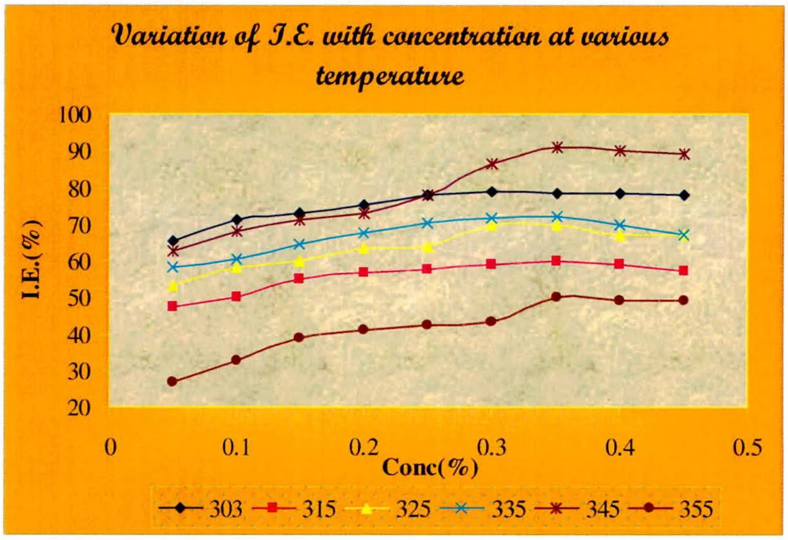


Fig-8

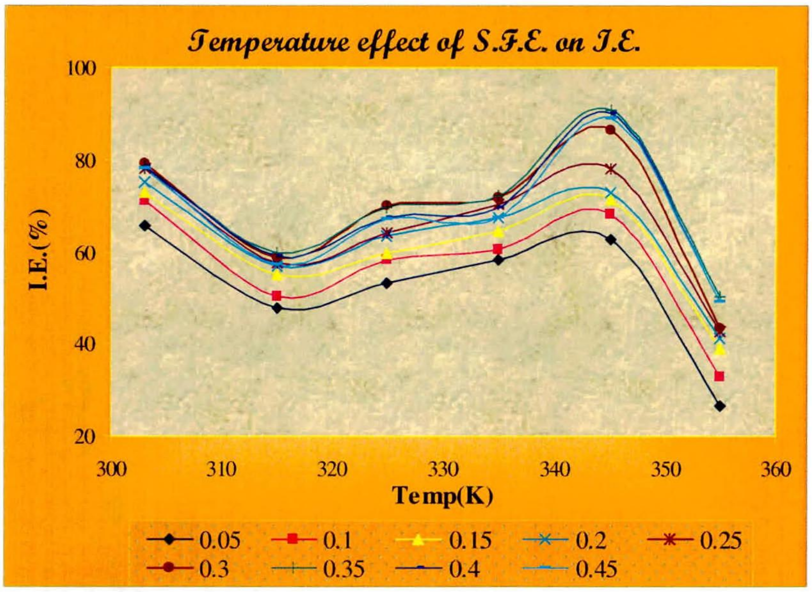


Table-4

Temperature effect on corrosion rate and IE for S.F.E. in HCl

Conc. (%)	Temperature(K)											
	303		315		325		335		345		355	
	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)	C.R. mpy	IE (%)
Blank	893	-	1000	-	1645	-	4772	-	14138	-	20086	-
0.05	307	65.6	523	47.6	768	53.3	1993	58.2	5252	62.8	14738	26.6
1	256	71.3	496	50.3	686	58.2	1884	60.5	4509	68.1	13502	32.7
0.15	241	72.9	449	55.1	656	60.0	1685	64.6	4039	71.4	12253	38.9
0.2	220	75.3	429	57.0	600	63.5	1543	67.6	3820	72.9	11805	41.2
0.25	196	78.0	421	57.8	588	64.2	1414	70.3	3098	78.0	11538	42.5
0.3	186	79.1	410	58.9	491	70.1	1339	71.9	1890	86.6	11335	43.5
0.35	192	78.4	400	59.9	496	69.8	1326	72.2	1273	90.9	9967	50.3
0.4	192	78.4	407	59.2	536	67.4	1443	69.7	1383	90.2	10146	49.4
0.45	195	78.1	429	57.1	538	67.3	1553	67.4	1528	89.1	10169	49.3

Adsorption behaviour

It is generally accepted that the organic molecules inhibit corrosion by adsorption at the metal/solution interface and that the degree of adsorption depends on the molecules chemical structure, chemical composition of the solution, the nature of metal surface, the temperature and the electrochemical potential at the metal/solution interface. [O.L.Riggs, 1973]

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metal has been deduced in terms of adsorption characteristics of the inhibitor. The surface coverage (θ) values are very useful while discussing the adsorption characteristics. The adsorbed layer acts as a barrier between the metal surface and the aggressive solution, leading to a decrease in the corrosion rate. It follows that the inhibition efficiency (IE) is directly proportional to the fraction of the surface covered (θ) by the adsorbed molecules. Therefore, (θ) is calculated using the relation θ = IE/100. The mode of variation of (θ) with the inhibitor concentration specifies the adsorption isotherm that describes the system.

Adsorption isotherm provides a clue to the mode and mechanism of adsorption. The surface coverage (θ) values for different concentrations of the inhibitors in acid medium were evaluated from the weight loss data. Attempts were made to fit data obtained from weight loss measurement into different adsorption isotherms like Langmuir and Temkin. An assumption of Langmuir adsorption isotherm relates concentration of inhibitor in the bulk electrolyte to the degree of surface coverage according to following equation

$$\mathbf{Log\ [\theta / 1-\theta] = log\ K + log\ C}$$

From the above equation, if the assumptions of Langmuir are obeyed, a plot of log (θ/1-θ) Vs log C should give a straight line. Langmuir plot for the corrosion reaction of mild steel in the presence of leaf sheath and staminate flower extracts are shown by Fig (9 and 10). The fact that lines on the figures are linear and very close to each other confirms that Langmuir adsorption isotherm is applicable to the adsorption of different concentration of inhibitors under study within the temperature range of 303 – 355K. This Langmuir plot also confirms the adsorption behaviour of the inhibitor and also a monolayer adsorption on mild steel surface.

A straight line was obtained when the surface coverage was plotted against log C for the inhibitor. This shows that the adsorption of the inhibitors at the mild steel /

acidic solution interface obeys Temkin adsorption isotherm. The plots of θ *vs.* log C for both the inhibitors (leaf sheath and staminate flower extracts) are shown in Figure (11&12). The surface coverage data were also tested by statistical calculations. Statistical estimation of correlation for the curve fitting of isotherms has been used to investigate the goodness of fit of the isotherms. The values of correlation co-efficients for the isotherms tested are given in table-5. The correlation values are almost 1 showing that the data obey both Langmuir and Temkin isotherms.

Table-5

Values of Correlation Coefficient obtained using adsorption isotherms for MS

Isotherms	**Correlation Coefficients**					
	L.S.E					
	303K	**315K**	**325K**	**335K**	**345K**	**355K**
Langmuir	0.918371	0.972413	0.970921	0.941736	0.986389	0.985781
Temkin	0.920169	0.974636	0.97222	0.944955	0.989259	0.981492
	S.F.E.					
Langmuir	0.966669	0.935397	0.940117	0.880496	0.906667	0.985068
Temkin	0.966621	0.935633	0.946519	0.888311	0.943477	0.982673

Fig-9

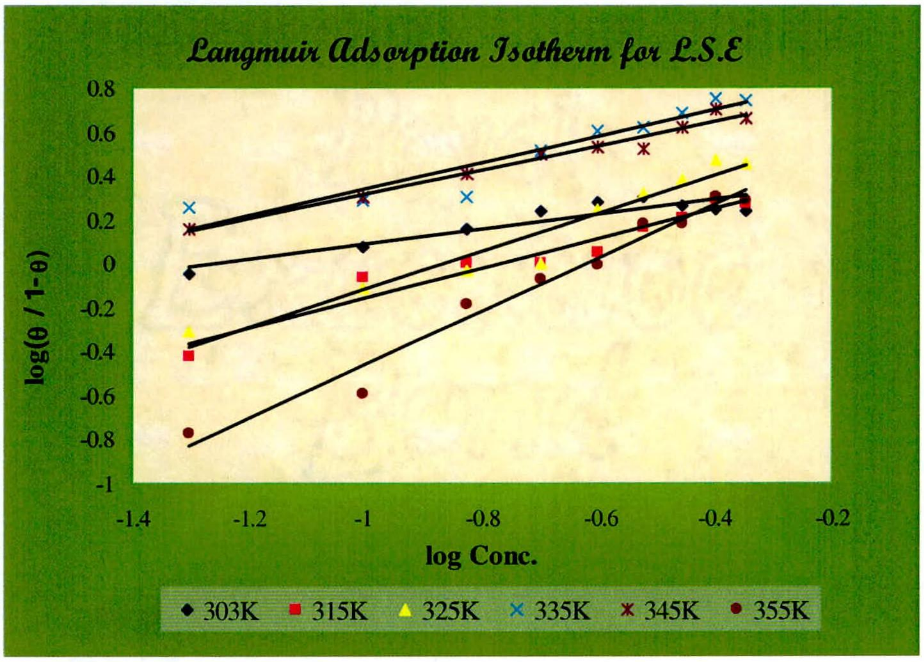

Langmuir Adsorption Isotherm for L.S.E
log(θ / 1-θ)
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.4
-1.2
-1
-0.8
-0.6
-0.4
-0.2
log Conc.
◆ 303K
■ 315K
▲ 325K
× 335K
✱ 345K
● 355K

Fig-10

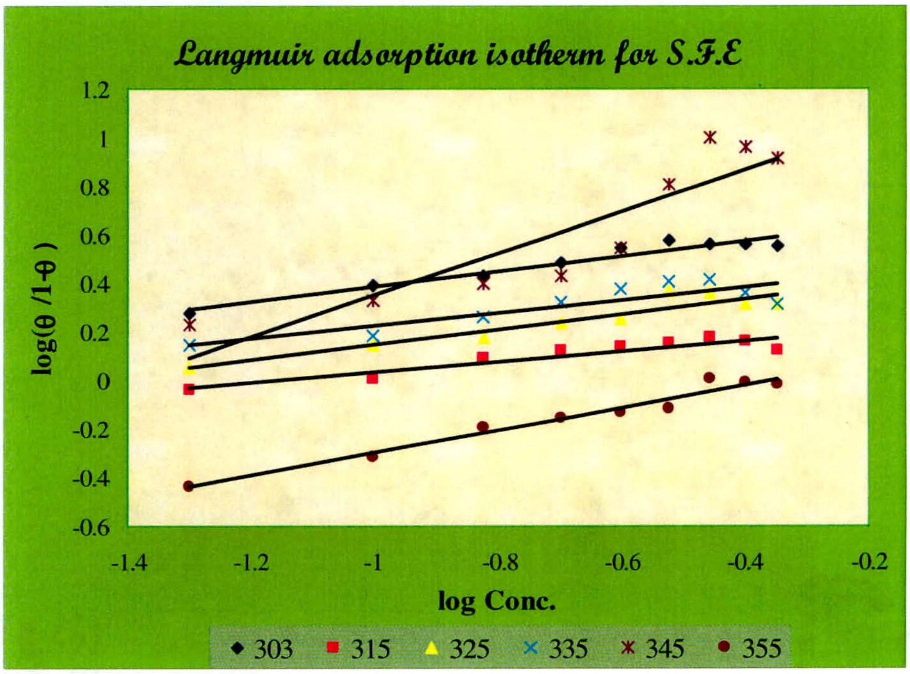

Langmuir adsorption isotherm for S.F.E
log(θ /1-θ)
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-1.4
-1.2
-1
-0.8
-0.6
-0.4
-0.2
log Conc.
◆ 303
■ 315
▲ 325
× 335
✱ 345
● 355

Fig-11

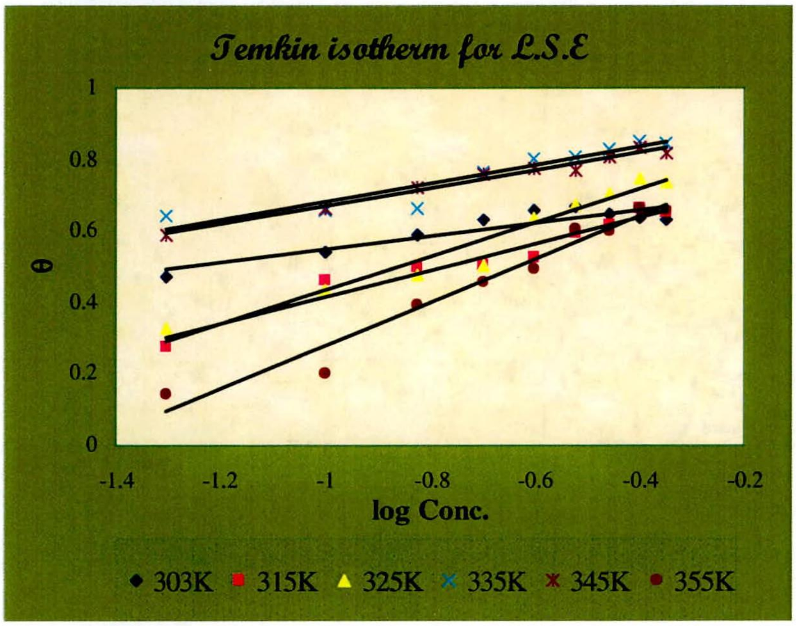
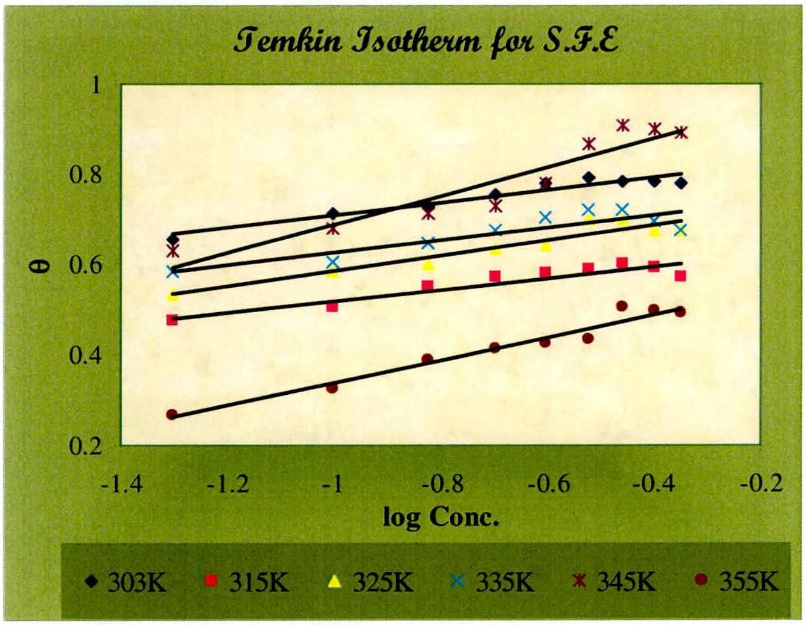

Temkin isotherm for L.S.E
θ
1
0.8
0.6
0.4
0.2
0
-1.4
-1.2
-1
-0.8
-0.6
-0.4
-0.2
log Conc.
◆ 303K ■ 315K ▲ 325K × 335K ✱ 345K ● 355K

Fig-12


Temkin Isotherm for S.F.E
θ
1
0.8
0.6
0.4
0.2
-1.4
-1.2
-1
-0.8
-0.6
-0.4
-0.2
log Conc.
◆ 303K ■ 315K ▲ 325K × 335K ✱ 345K ● 355K

Activation energy (E_a)

The activation energy at different concentration of the inhibitor in HCl was calculated by plotting log C.R *vs.* 1/T (fig 13&14). The dependence of logarithm of the corrosion rate on the reciprocal values of the absolute temperature gives a straight line. The values of the slope of these straight lines permit the calculation of activation energy Ea by the application of following equation,

$$\mathbf{C.\ R = A.\ e^{(-Ea\,/\,RT)}}$$

Where *A* is the frequency factor for the reaction, *R* is the universal gas constant; *T* is the temperature (Kelvin). Thus *Ea* can be evaluated from the rate constant at any temperature. The estimated values of E_a for MS in leaf sheath and staminate flower extracts in 1M HCl are listed in the tables (6&7).From the table it is understood that energy of activation changes in the presence of the inhibitor. The estimated E_a in the presence of inhibitors infer that the interaction between the metal surface and the current inhibitors under study was found to be strong enough to prevent corrosion.

This may seem surprising and paradox, but Riggs et al., (1967) reported that in the presence of adsorbed inhibitor, the dissolution of the metal proceeds with two distinct processes corresponding to the covered area and the bare metal surface concluded that at high degree of coverage the dissolution process is not only determined by the reaction of the metal from the bare surface but also involves the adsorbed inhibitor and consequently the E_a can assume values greater or smaller than those calculated in the absence of the inhibitor.

As far as the present study is concerned, the above said explanation aptly suits the results obtained for the leaf sheath and staminate flower extracts. It has also been pointed out by Khamis et al., (1990) that a corrosion inhibitor greatly enhances the activation energy of the corrosion.

Experiments conducted by Bag et al., (1996) also reflected lower E_a values for the inhibited systems. Studies carried out by Taha et al., (1995) revealed that the presence of inhibitors decreased the E_a of the reaction to an extent depending on the nature of inhibitor.

It was also found that the activation energies were lower than the value of 80 KJ/mol required for chemical adsorption confirming that the adsorption of the extract of leaf sheath and staminate flower occurred through the mechanism of physical adsorption.

Fig-13

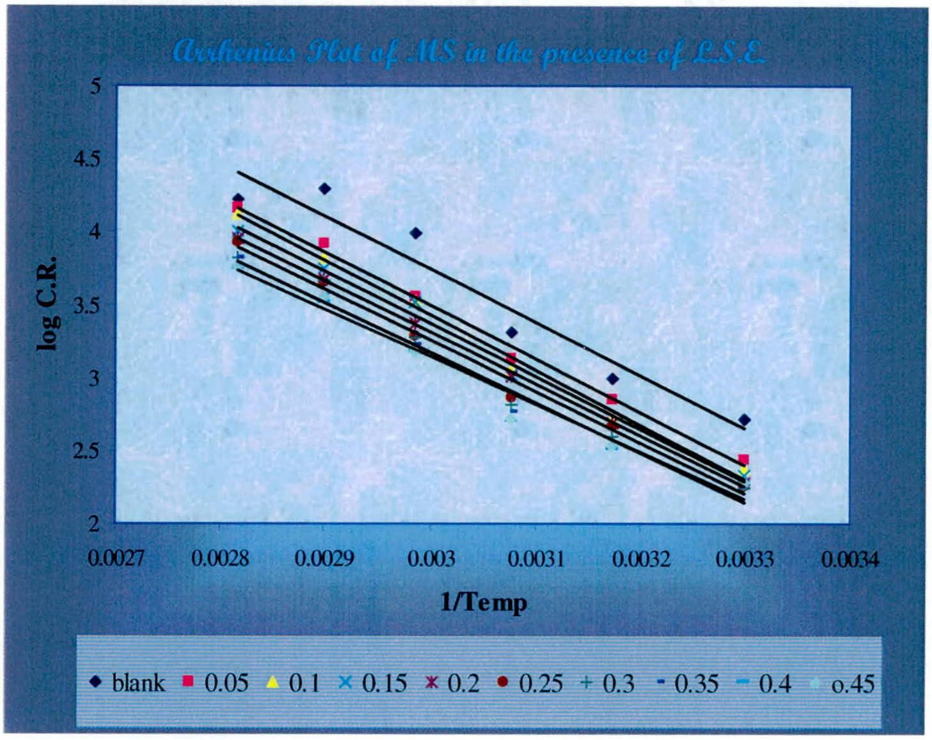
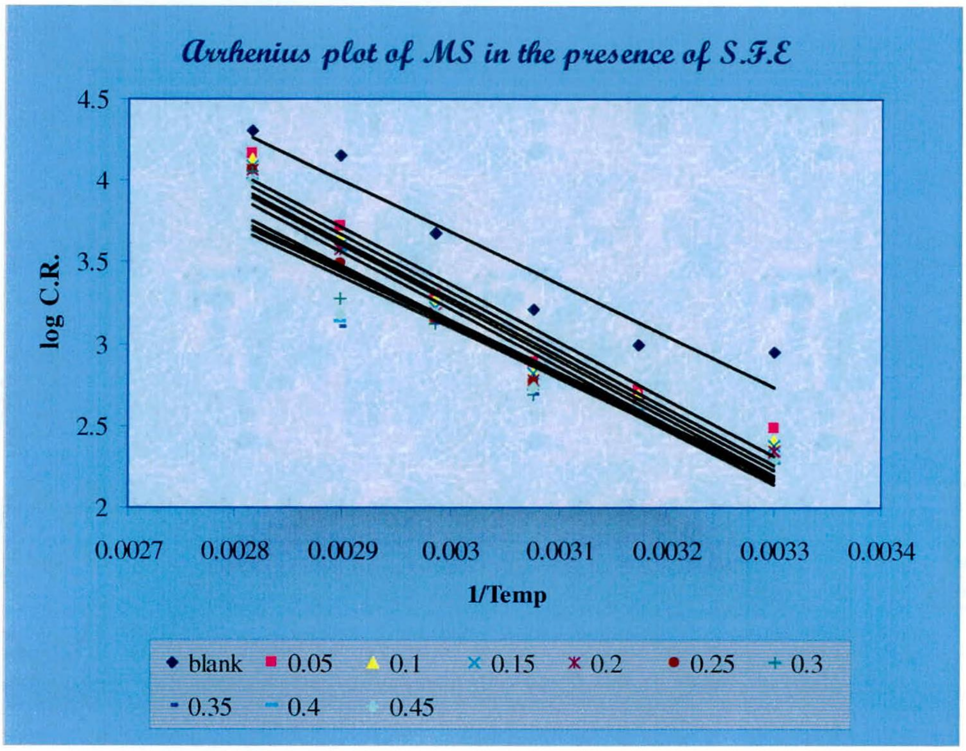


Fig-14



Temperature studies result help in the calculation of thermodynamic parameters like standard free energy of adsorption (ΔG), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS). The results of thermodynamic parameters are calculated for L.S.E. and S.F.E. adsorption on mild steel in HCl medium are reported in table 6&7.

Free energy of adsorption

Free energy of adsorption (ΔG) was calculated by using the standard equation

$$\mathbf{Log\ C=log\ (\theta/1-\theta)-log\ B}$$

Where $\log B= -1.74-(-\Delta G/2.303RT)$

C= inhibitor concentration

The plot of log ($\theta/1-\theta$) against log C, for the inhibitors under study was linear showing an adsorption on the metal surface according to the Langmuir isotherm [Langmuir]. The negative values obtained for ΔG suggest the strong interaction of the inhibitor molecules whereas low value of ΔG indicated spontaneous adsorption of inhibitors on MS surface. Two modes of adsorption can be considered. The process of physical adsorption requires the presence of electrically charged metal surface and the charged species in the bulk of the solution. Chemisorption process involves charge sharing or charge transfer from the inhibitor molecules to the metal surface. These values were negatively less than the threshold value of -40KJ/mol required for chemical adsorption hence the adsorption of the extracts of leaf sheath and staminate flower on the surface of mild steel is physical adsorption. The obtained value of ΔG (Table 6and 7) suggests a strong physical adsorption of both the extracts components onto the steel surface in HCl solution and it is spontaneous.

Enthalpy and Entropy of adsorption

Enthalpy of adsorption and Entropy of adsorption were calculated from the following equation

$$\mathbf{\Delta G = \Delta H - T\Delta S}$$

The intercept (ΔH) and slope (ΔS) obtained from the plot -ΔG vs T (fig 15 and 16) were listed in the table (6 and 7)This agrees with general suggestion that more negative values of ΔG and positive value of ΔS leads to increase in inhibitor efficiency [Sanyal S., 1990]. The negative values of ΔH obtained in this study indicate that the adsorption of leaf sheath and staminate flower extract molecules is an exothermic reaction. The values for the heat of adsorption for both the inhibitors in

HCl were found to be less than (40 KJ/mol). This indicates all the inhibitors were adsorbed physically. The positive values of entropy of adsorption ΔS suggest the adsorption to be a spontaneous process and the change in entropy was found to be greater than zero. This indicates that the reaction is irreversible. It is clear that, the complete desorption of the inhibitor is not possible.

Fig-15

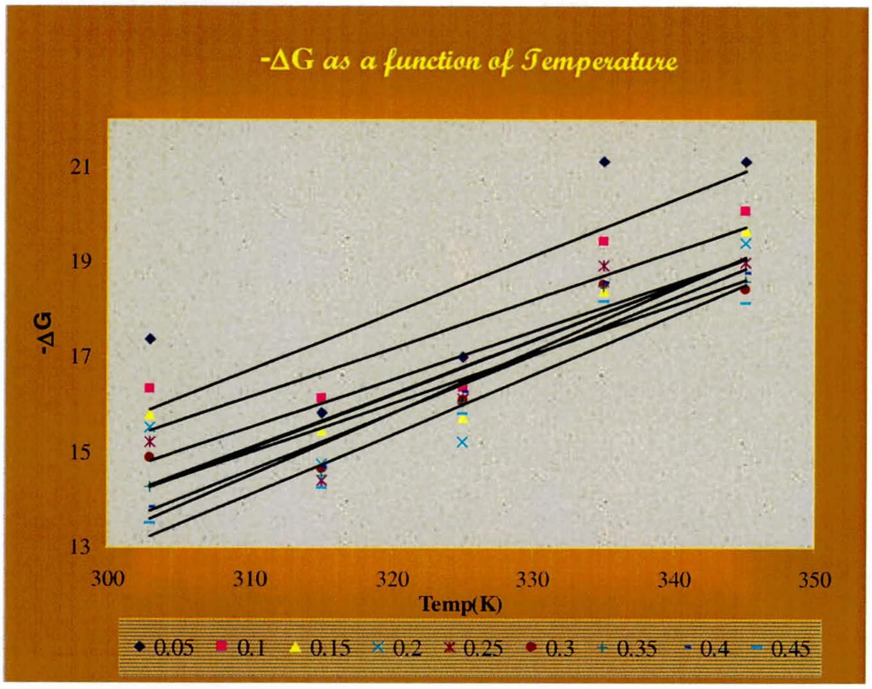


Fig-16

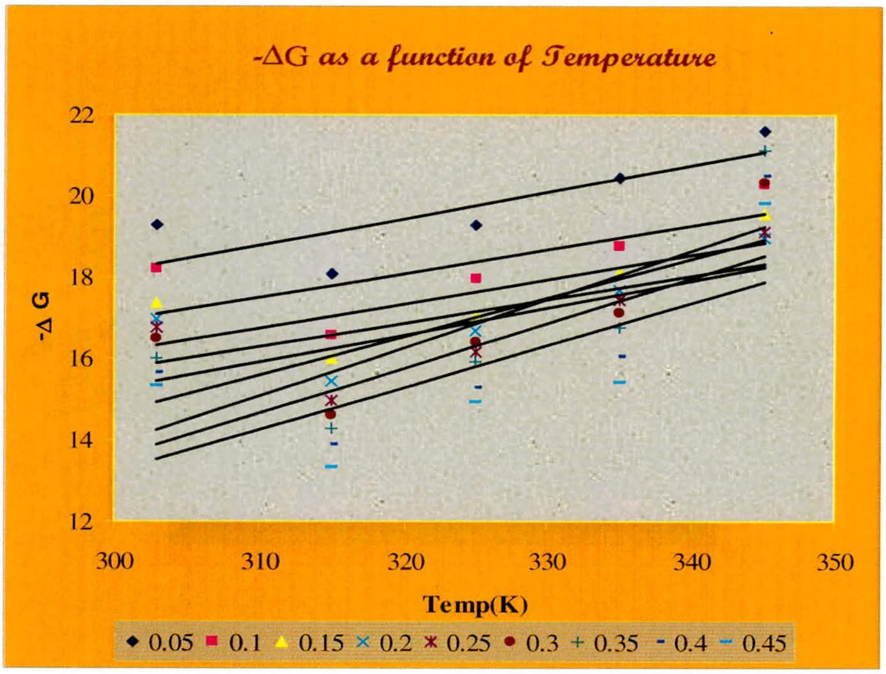


Table -6

Kinetic and thermodynamic parameter of MS in presence of L.S.E. in 1M HCl

Conc. (%)	Activation energy (Ea) KJ/mol	Free energy of adsorption (-ΔG) KJ/mol						Heat of adsorption (ΔH) KJ/mol	Entropy change (ΔS) KJ/mol
		305K	315K	325K	335K	345K	355K		
Blank	69.70	-	-	-	-	-	-	-	-
0.05	69.78	17.38	15.81	16.99	21.13	21.10	15.40	-20.45	11.99
1	71.53	16.34	16.13	16.35	19.42	20.07	14.56	-15.38	10.18
0.15	68.99	15.79	15.45	15.73	18.38	19.66	16.14	-15.68	10.06
0.2	67.05	15.51	14.74	15.20	18.93	19.41	16.10	-19.95	11.31
0.25	67.14	15.22	14.42	16.12	18.91	19.00	15.88	-20.26	11.39
0.3	66.10	14.88	14.65	16.09	18.51	18.41	16.62	-17.15	10.37
0.35	65.30	14.26	14.50	16.07	18.48	18.61	16.13	-22.83	12.08
0.4	61.54	13.85	14.69	16.25	18.54	18.75	16.58	-26.04	13.08
0.45	61.96	13.50	14.24	15.81	18.15	18.13	16.15	-24.99	12.61

Table-7

Kinetic and thermodynamic parameters during adsorption of inhibitor on MS surface in S.F.E. in 1M HCl

Conc. (%)	Activation energy (Ea) KJ/mol	Free energy of adsorption (-ΔG) KJ/mol						Heat of adsorption (ΔH) KJ/mol	Entropy change (ΔS) KJ/mol
		305K	315K	325K	335K	345K	355K		
BLANK	60.08	-	-	-	-	-	-	-	-
0.05	66.67	19.26	18.08	19.28	20.42	21.59	17.67	-1.46	6.53
1	67.33	18.18	16.55	17.94	18.76	20.27	16.49	-0.86	5.91
0.15	66.61	17.36	16.00	17.05	18.12	19.56	16.09	-2.03	6.05
0.2	67.18	16.95	15.44	16.67	17.69	18.95	15.52	-1.62	5.78
0.25	66.84	16.77	14.94	16.15	17.42	19.10	15.02	-4.53	6.59
0.3	63.96	16.48	14.59	16.38	17.13	20.30	14.60	-13.82	9.49
0.35	59.21	15.98	14.29	15.92	16.74	21.10	14.96	-21.70	11.86
0.4	60.02	15.65	13.86	15.26	16.03	20.49	14.46	-19.59	11.04
0.45	60.47	15.31	13.33	14.93	15.40	19.81	14.10	-17.70	10.30

Polarization measurement

Potentiodynamic polarization results

Electrochemical measurements were carried out using sophisticated instrument, Solartron 1280 B. To evaluate the effect of the leaf sheath and staminate flower extract on the electrochemical behaviour of mild steel, cathodic and anodic polarization experiments were carried out. Electrochemical corrosion parameters such as corrosion current density I_{corr}, corrosion potential E_{corr} and inhibition efficiency (IE %) are given in the table (8&9). the following observations were deduced from the table

- Decrease in I_{corr}
- No significant changes in E_{corr}
- Changes in b_a and b_c
- Increase in R_p value

The decreases in I_{corr} values infer that the inhibitors in the present investigation are adsorptive type. In the presence of inhibitors there was no significant change in corrosion potential (E_{corr}) which suggests that both the inhibitors are mixed type inhibitor by controlling both anodic and cathodic reactions. Potentiodynamic curves of mild steel in the presence of inhibitors indicate that the inhibitors control hydrogen evolution as well as metal dissolution. Inhibition efficiency calculated using I_{corr} and R_p indicate that inhibition efficiency increases with increasing concentration of the extract and maximum inhibition efficiency was found to be 88.58% and 76.37% using I_{corr} values and R_p values for L.S.E., similarly for S.F.E. it was 75.06% and 62.45%. Changes in Tafel constants b_a and b_c with the concentration of the inhibitors confirm that they are mixed type. In all concentrations b_a is greater than b_c suggesting that though the inhibition is under mixed control, the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.

Table -8

Corrosion parameters of MS in the presence of L.S.E. in HCl

Conc. Of L.S.E (%)	-Ecorr X (10^{-3}) (Volts)	Icorr X (10^{-4}) (Amp/cm^2)	ba (mV/ dec)	bc (mV/ dec)	IE (%)	Rp Ohm/ cm^2	IE (%)
Blank	513	184.45	254.64	183.16	-	2.55	-
0.05	515	55.741	175.07	131.75	69.7	5.89	56.6
0.1	511	49.165	165.67	127.63	73.3	6.41	60.1
0.15	509	39.035	152.7	120.54	78.8	7.58	66.3
0.2	509	34.979	146.98	119.23	81.0	8.16	68.6
0.25	508	24.003	129.9	110.35	86.9	9.48	73.0
0.35	506	21.059	120.48	98.713	88.5	10.81	76.3

Fig -17

Polarization curves of MS in the presence of L.S.E. in acid medium

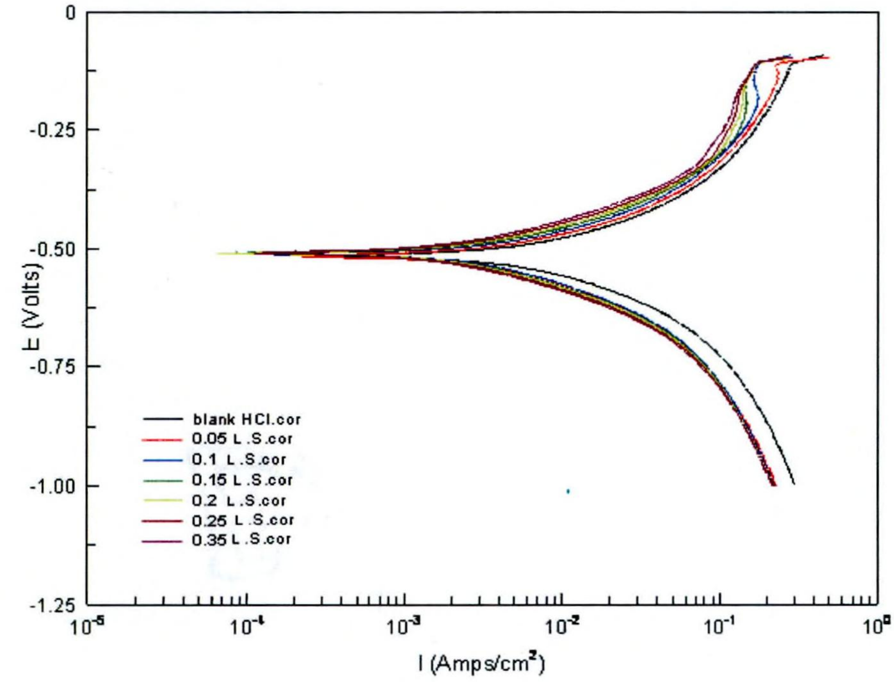


Fig -18

Polarization curves of MS in the presence of S.F.E. in acid medium

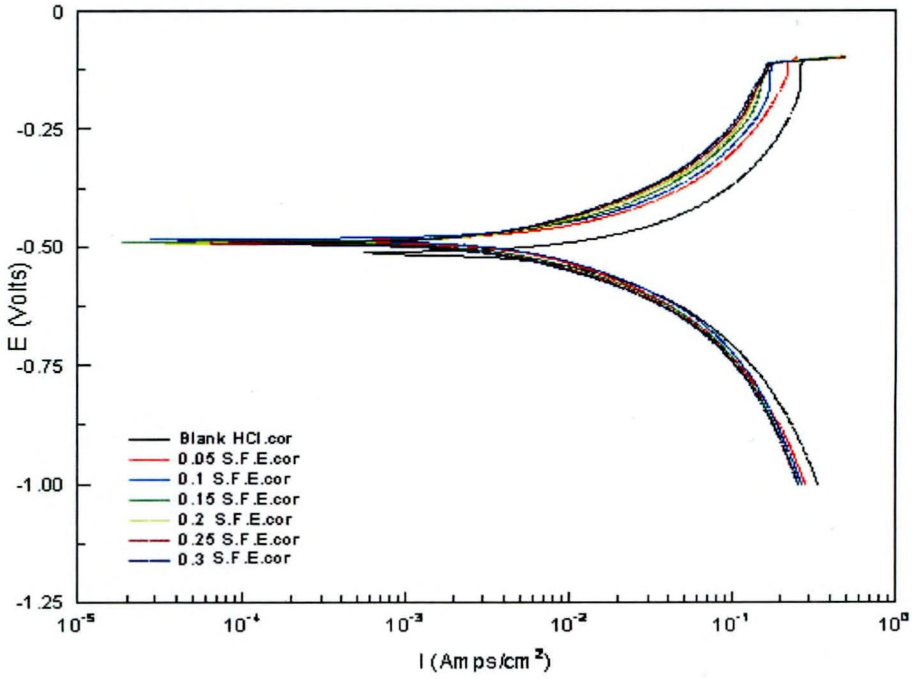


Table -9

Electrochemical data by Linear and Tafel polarization for corrosion of MS in the presence of S.F.E. in HCl

Conc. Of S.F.E (%)	-Ecorr X (10^{-3}) (Volts)	Icorr X (10^{-4}) (Amp/cm^2)	ba (mV/ dec)	bc (mV/ dec)	IE (%)	Rp Ohm/ cm^2	IE (%)
Blank	513	184.45	254.64	183.16	-	2.55	-
0.05	487	95.747	219.55	155.9	48.0	4.13	38.1
0.1	484	69.924	169.16	141.45	62.0	4.58	44.2
0.15	489	64.51	169.03	149.3	65.0	5.56	54.0
0.2	491	53.812	154.42	154.79	70.8	6.23	59.0
0.25	492	49.392	150.08	152.91	73.2	6.45	60.3
0.3	492	45.988	141.69	138.34	75.0	6.80	62.4

Electrochemical impedance studies

Electrochemical impedance studies (EIS) are an important tool to study the mechanism of inhibition process. The corrosion behaviour of mild steel in acid solution in the presence of leaf sheath and staminate flower extract in 1M HCl was investigated by EIS at room temperature .Various impedance parameters such as charge transfer resistance (R_{ct}), Double layer capacitance (C_{dl}) and the corresponding IE calculated are given in the table (10&11). Impedance diagram (Nyquist plot) obtained for mild steel in 1 M HCl in the presence of various concentrations of the inhibitors are depicted in Figure (19 & 20). From the impedance parameters, it can be seen that as the L.S.E and S.F.E concentration increases, R_{ct} values were found to increase. The figure illustrates that the charge transfer resistance is found to increase with increase in concentration of the inhibitor. This indicates the dissolution of the metal and the corrosion of mild steel is controlled by charge transfer process. The charge transfer reactions are known to take place at the metal solution interface. Consequently the high R_{ct} values of inhibited electrodes can be explained by the build up of protective layers and the effective barrier behaviour of adsorbed layers. The C_{dl} values tend to decrease with increase in concentration of L.S.E and S.F.E. The decrease in C_{dl} values indicates the adsorption of L.S.E and S.F.E molecule on the metal surface. Decrease in C_{dl} can result from a decrease in local dielectric constant or an increase in thickness of the electrical double layer, suggests that the inhibitors function by adsorption at the metal solution interface [Mc. Cafferty E.,1972].

Table -10

Impedance parameters of MS in the presence of L.S.E. in HCl

Conc. Of L.S.E (%)	R_{ct} Ω cm^2	IE (%)	C_{dl}x10^{-5}μF	θ
Blank	9.2	-	60.1	-
0.05	32.4	71.4	25.6	0.57
0.1	44.8	79.3	35.0	0.41
0.15	48.6	80.9	34.1	0.43
0.2	58.3	84.1	33.3	0.44
0.25	64.7	85.6	30.8	0.48
0.35	66.6	86.0	28.7	0.52

Table -11

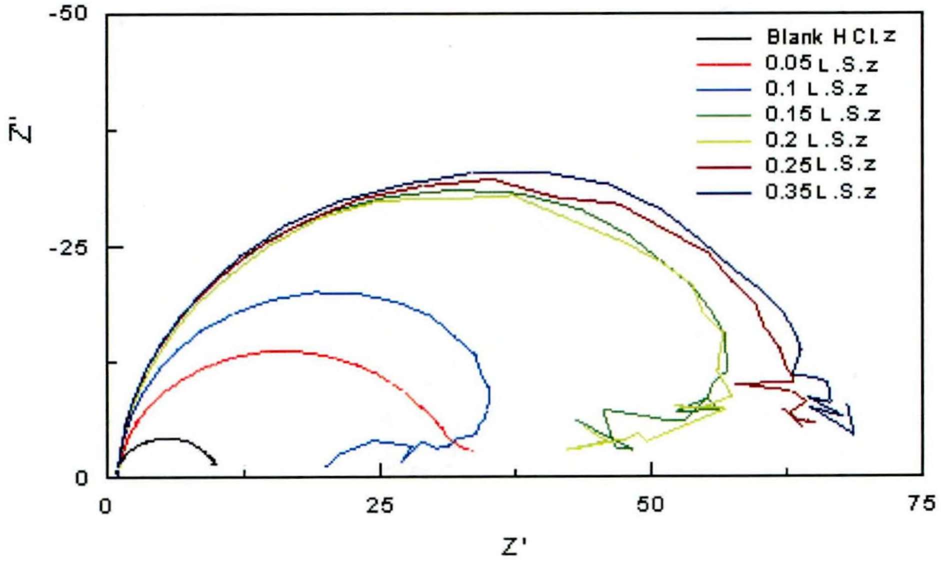
Impedance parameters of MS in the presence of S.F.E. in HCl

Conc. Of S.F.E (%)	R_{ct} Ω cm^2	IE (%)	C_{dl}x10^{-5} μF	θ
Blank	9.2	-	60.1	-
0.05	13.5	31.6	39.5	0.34
0.1	20.9	55.8	38.1	0.36
0.15	23.4	60.4	35.4	0.41
0.2	27.1	65.8	34.4	0.42
0.25	27.4	66.2	29.0	0.51
0.3	28.7	67.7	28.4	0.52

Fig -19

Impedance behaviour of MS in the presence of L.S.E.

Nyquist Plot



Bode Plot

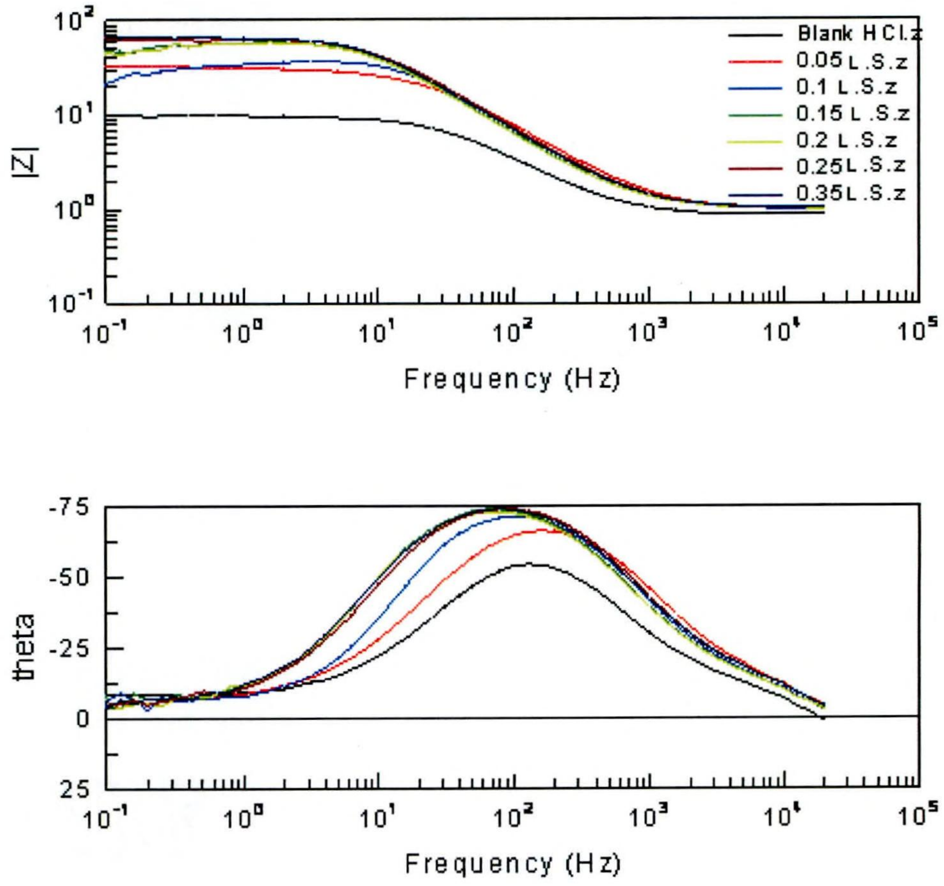
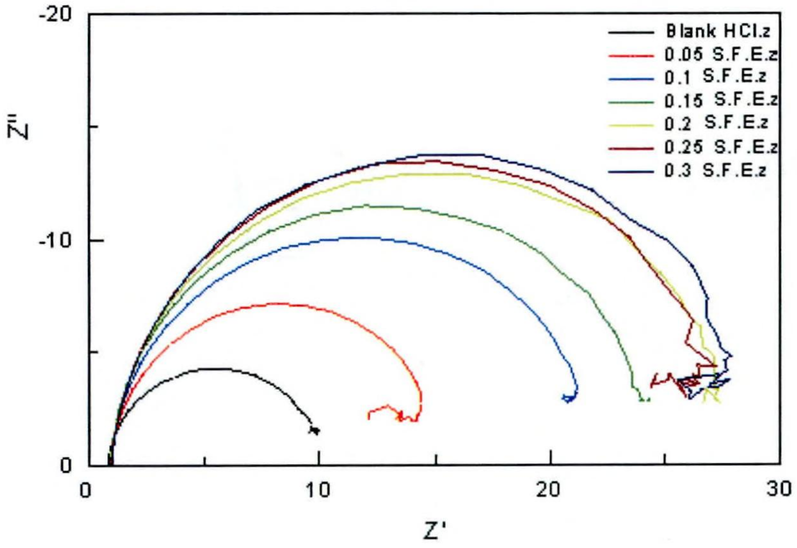


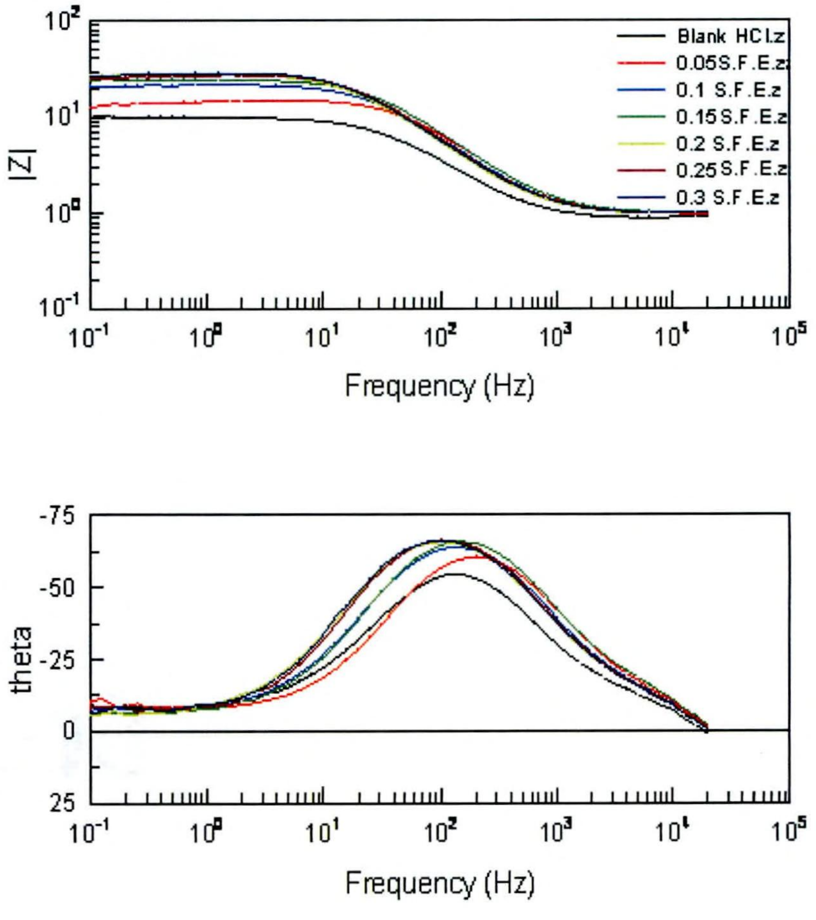
Fig -20

Impedance behaviour of MS in the presence of S.F.E.

Nyquist Plot



Bode Plot



Weight loss Vs Electrochemical method

The values of inhibition efficiency calculated from electrochemical measurements are lower than those obtained from weight loss data. Nevertheless in general, the polarization data confirms the results of steel dissolution measurements. The difference in inhibition efficiency by different techniques can be attributed to the fact that weight loss method gives average corrosion rates, while electrochemical measurements give instantaneous corrosion rate. The difference may be expected to arise because of the difference in time required to form an adsorbed layer, which brings down corrosion.

Fig -21

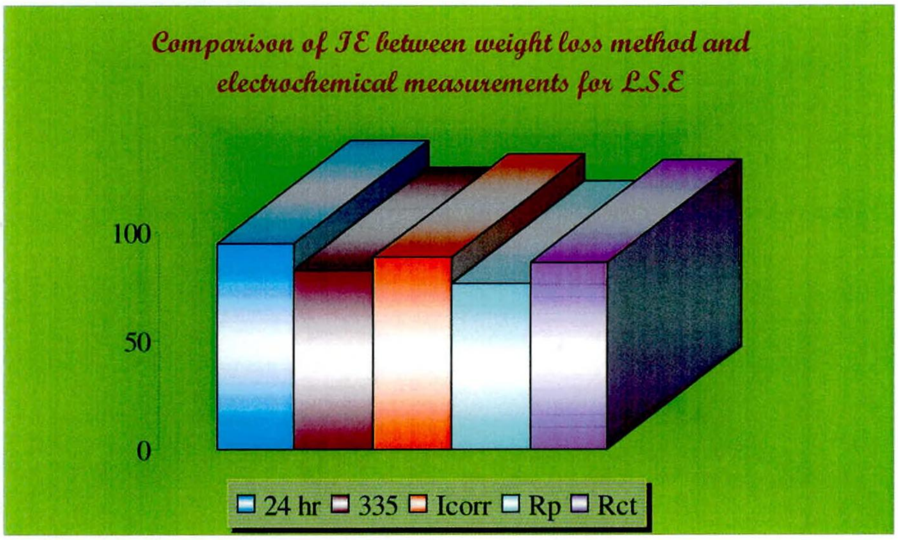


Fig -22

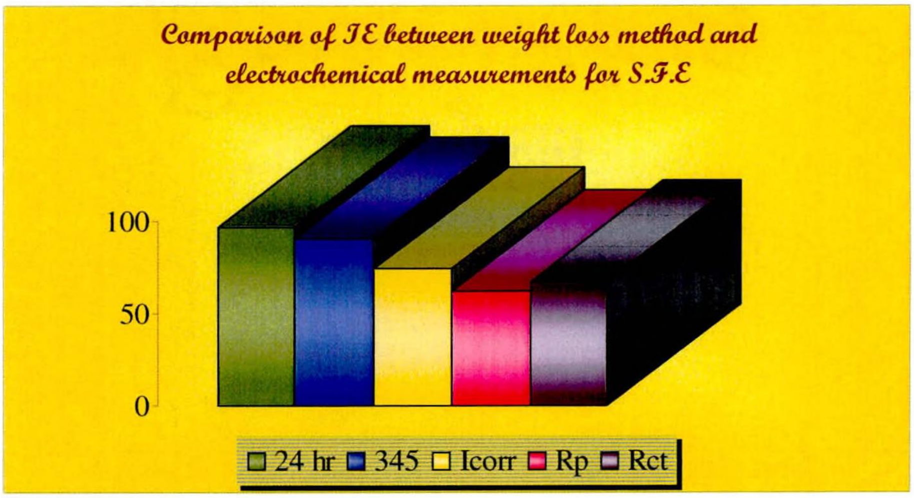


Fig 21 and 22 depict the performance of L.S.E. and S.F.E. by weight loss and electrochemical measurements.

Shelf life of the extracts at room temperature and at refrigerated condition

Natural inhibitors are estimated by their stability, consistent performance and biodegradability. To test the consistent performance of the extracts under study, weight loss experiments were conducted for a period of 3months. The extracts were stored at room temperature and in refrigerator. The results are presented in the table-12 and fig (23 and 24)

No fungal growth was noticed in the extracts at both storage conditions. There was no unfavourable odour, or release of toxic gases during storage. The data in table revealed that the inhibition efficiency slowly decreased during storage. This may be due to some chemical reactions between the constituents. Due to the reactions the active groups responsible for the adsorption on the MS surface may not be available for adsorption. Therefore the total surface covered decreased showing decline of inhibition efficiency. 75% of inhibition efficiency after 3 months is appreciable. Both extracts showed almost same efficiency which confirms that they can be stored at room temperature itself. Their performance may be maintained by adding suitable stabilizing agents. Both extracts have reasonable 'shelf life'.

Table -12

Shelf life of L.S.E. and S.F.E

Period of study (weeks)	IE %			
	L.S.E		S.F.E	
	R.T.	R.C.	R.T.	R.C.
1	98.0	94.7	96.4	90.9
2	96.7	92.3	92.8	89.1
3	94.3	89.6	91.9	88.8
4	92.6	87.9	86.6	87.4
5	88.5	86.4	85.8	87.0
6	87.8	81.9	84.1	84.2
7	86.8	77.8	83.2	82.2
8	80.8	76.9	82.9	79.0
9	77.7	74.3	79.5	75.5
10	76.3	73.1	77.8	72.6

Fig -23

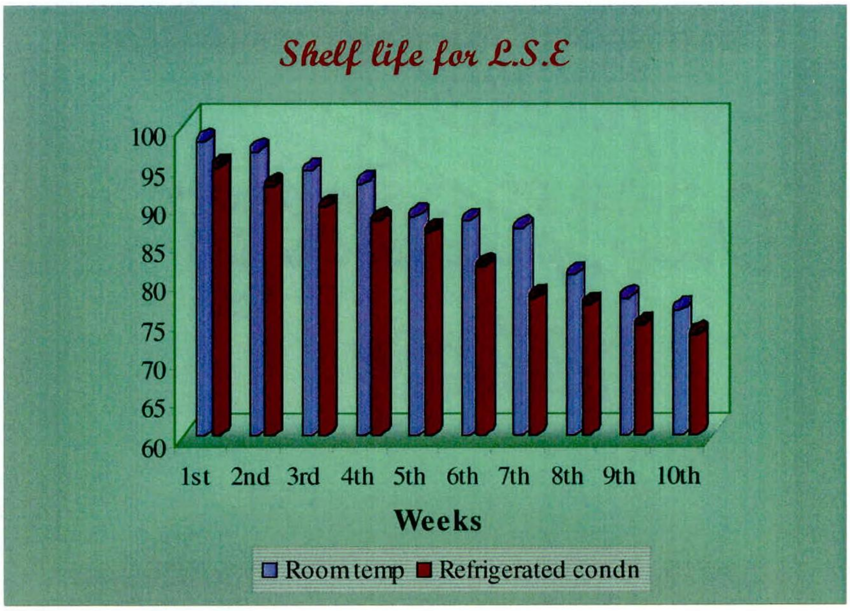
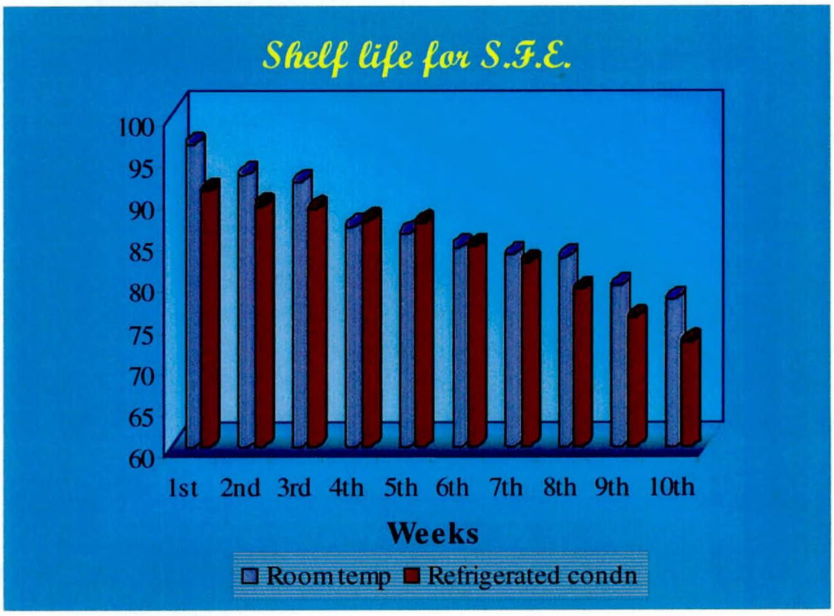

Shelf life for L.S.E
100
95
90
85
80
75
70
65
60
1st
2nd
3rd
4th
5th
6th
7th
8th
9th
10th
Weeks
Room temp
Refrigerated condn

Fig -24

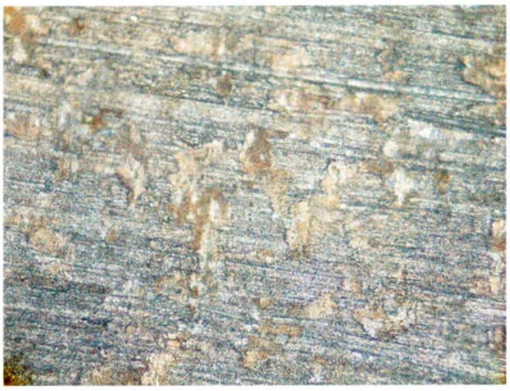

Shelf life for S.F.E.
100
95
90
85
80
75
70
65
60
1st
2nd
3rd
4th
5th
6th
7th
8th
9th
10th
Weeks
Room temp
Refrigerated condn

Optical electron microscope

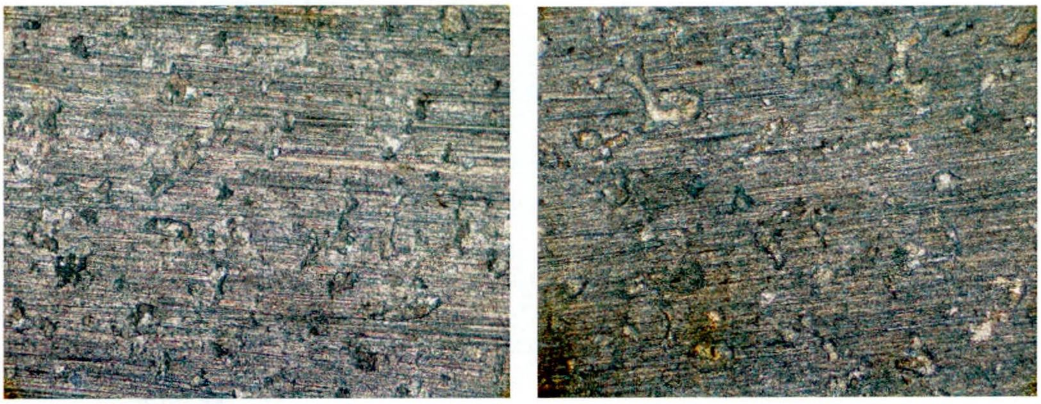
Optical electron microscope was used to evaluate the change in the surface morphology caused by the contact with the acid solutions and to monitor the effect of addition of the inhibitors.

The test specimens which were immersed in the blank (1 M HCl) and in the inhibitors L.S.E. and S.F.E. for 3hrs were observed under an optical electron microscope and photomicrographs are shown in the figure 25. After pickling in HCl with and without inhibitor, red, orange areas are apparent on the MS surfaces. These are attributable to an intensified corrosive attack of the pickling solution with local etching of the steel surface. Samples pickled without inhibitor (Photomicrograph 25a) show an overall attack upto 80 percent of MS surface which was reduced to about 10 to 20 percent by the addition of inhibitor (Photomicrographs 25b and 25c).

Fig -25



Photomicrograph of MS in presence of HCl (25a)



Photomicrographs of MS in presence of L.S.E. (25b) and in presence of S.F.E. (25c)

FT-IR technique

Leaf Sheath Extract

Cellulose and lignin are the main phytochemical constituents of the acid extract of Leaf Sheath of coconut. The chemical structure of these compounds contain electron rich bond or hetero atoms that facilitate their electron donating ability, and hence the inhibition of corrosion of mild steel. This fact is further confirmed from the IR spectral data (table -13).

The FT-IR spectrum taken using the extract (fig 26) shows the characteristic –OH absorption peaks at 3400-3200 cm^{-1} (broad) and at 1610.45 cm^{-1}. The band at 1035.7 cm^{-1} represents the primary alcoholic group.

In FT-IR spectra taken using the adsorbed material of the extract on MS surface(fig 27) the broad band at 3400-3200 cm^{-1} is completely absent showing that the constituents of the extract are adsorbed on the metal surface through the –OH groups. It was found that the primary alcoholic band at 1035.7 cm^{-1} was shifted to 1041 cm^{-1} indicating that there is an interaction between the inhibitor and mild steel surface (Eddy et al., 2008).

Table-13

FT-IR spectral details of the L.S.E. concentrate and the adsorbed materials

Pure Extract		**Adsorbed material**	
Frequency	**Assignment**	**Frequency**	**Assignment**
3400-3200 cm^{-1} (broad)	**Hydroxy group H-bonded OH stretch**	**1041 cm^{-1}**	**Primary alcohol**
1610.45 cm^{-1}	**Primary amine**		
1035.7 cm^{-1}	**Primary alcohol**		

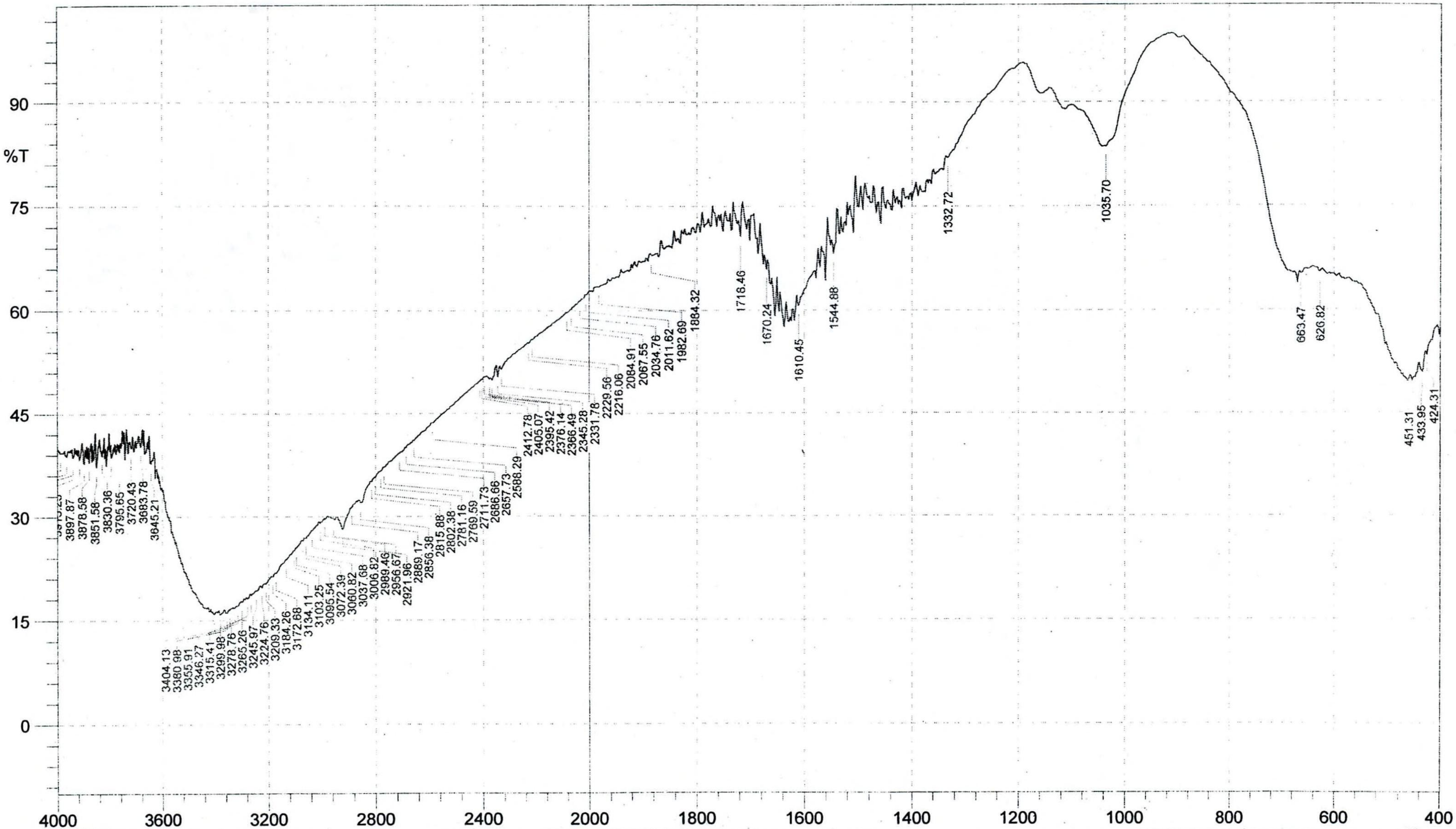


Fig-26
IR spectrum of acid extract of Leaf Sheath concentrate

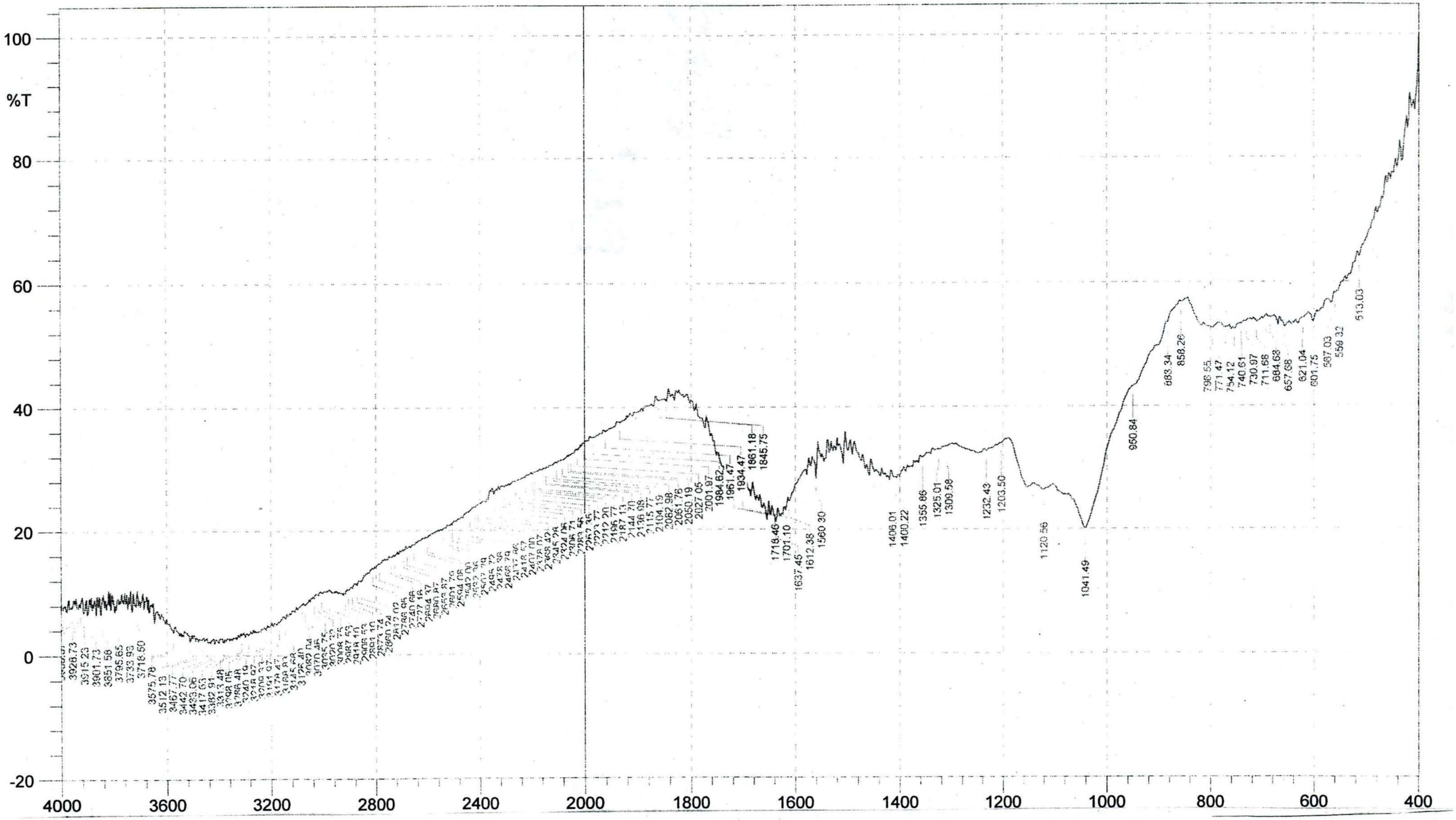


Fig-27
IR spectrum of the adsorbed material of mild steel in the presence of acid extract of Leaf Sheath as an inhibitor

Staminate flower extract

Characteristic IR absorption spectra of S.F.E. concentrate and the adsorbed material are shown in fig (28 and 29) respectively. The broad absorption bands at 3750-3200 cm^{-1} and at 1022 cm^{-1} in the extract spectrum confirms the presence of –OH group. The presence of primary amine is indicated by the absorption peak at 1629.74 cm^{-1} (table - 14).

The figure 29 revealed that the adsorbed material is not IR active. Frequencies of adsorption of –OH and amino groups were missing. This suggests that the adsorption of the inhibitor on the surface of mild steel might have occurred through the missing bonds (Ebenso et al., 2008).

Table-14

FT-IR spectral details of the S.F.E. concentrate and adsorbed materials

Pure Extract		**Adsorbed material**	
Frequency	**Assignment**	**Frequency**	**Assignment**
3750-3200 cm^{-1} (broad)	**Hydroxy group**	**804 cm^{-1}**	**Substituted aromatic ring**
1629.74 cm^{-1}	**Primary amine**		
1022 cm^{-1}	**Primary alcohol**		

From FT-IR technique, it is confirmed that the L.S.E. and S.F.E. are adsorbed on MS surface and form a protective blanketing layer. This could prevent the corrosion of MS in acid medium.

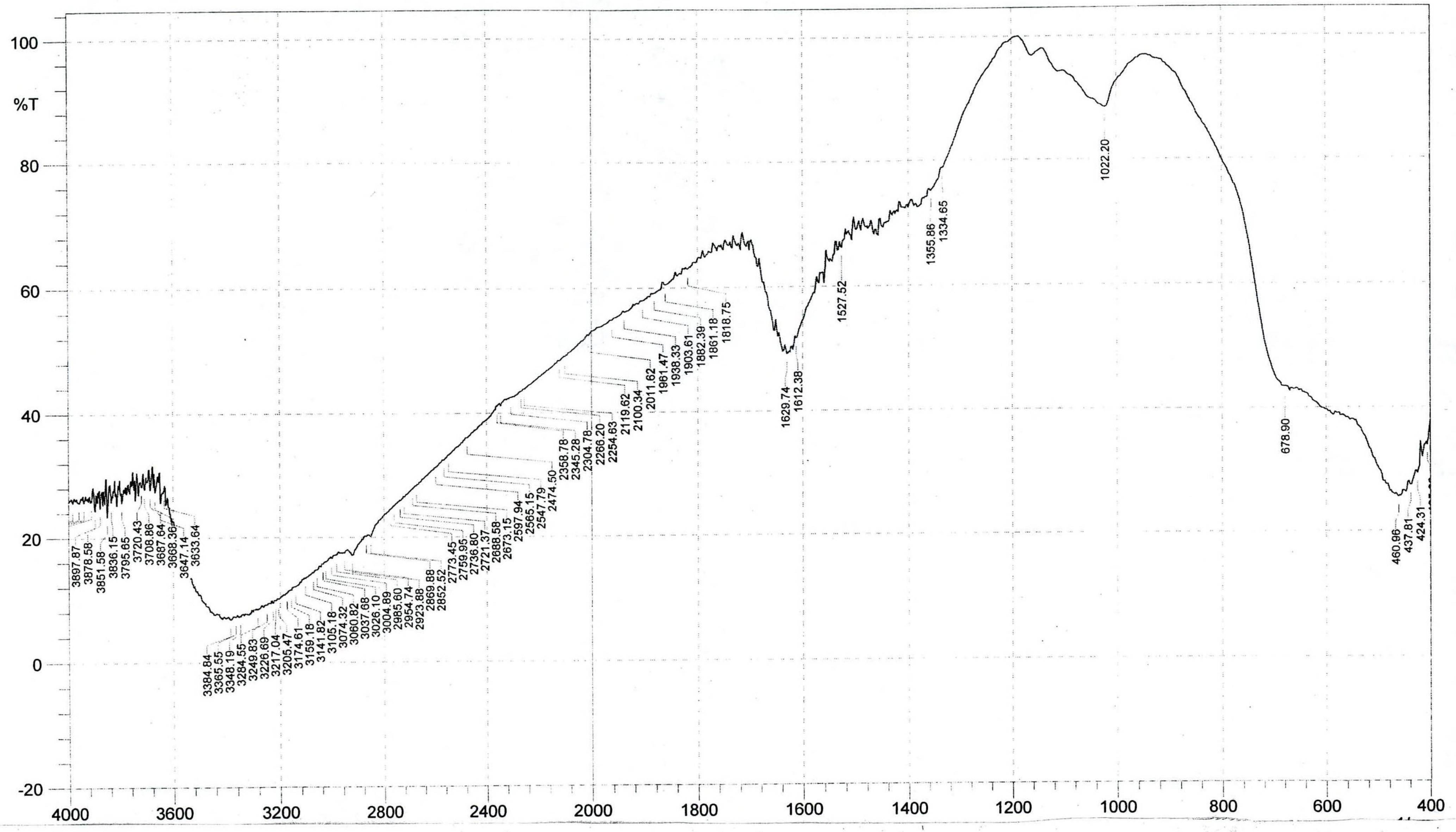


Fig-28
IR spectrum of acid extract of Staminate Flower concentrate

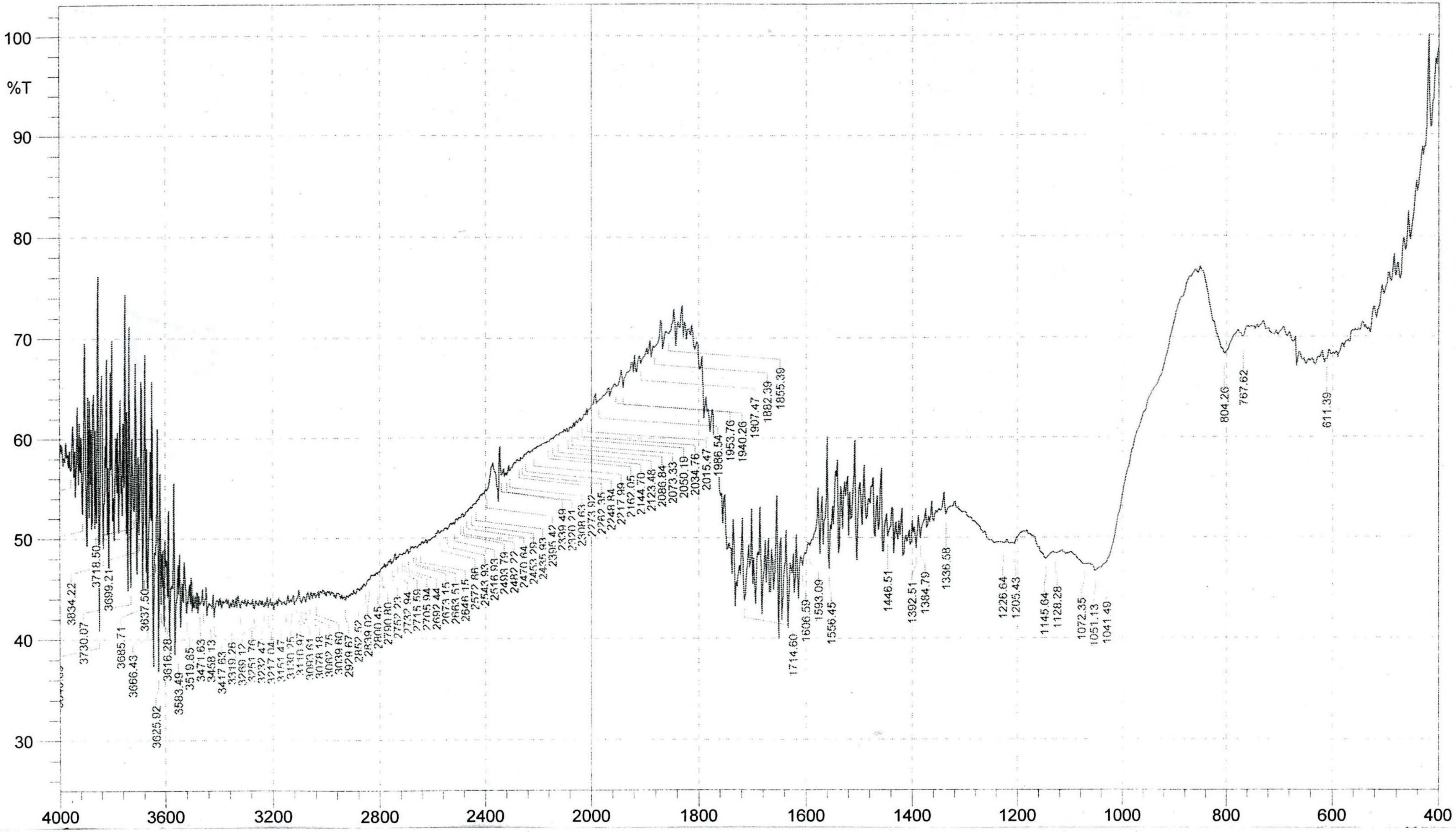


Fig-29

IR spectrum of the adsorbed material of mild steel in the presence of acid extract of Staminate Flower as an inhibitor

Mechanism

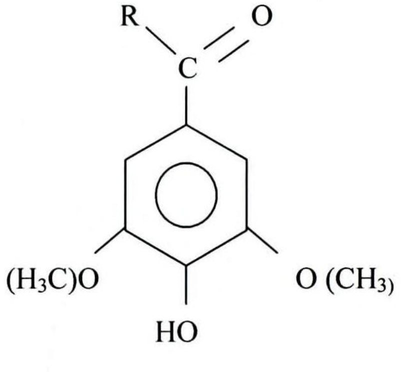
The extracts of L.S.E. and S.F.E. contain number of oxygen containing organic compounds. Adsorption of these compounds may occur through their active centre. The Langmuir and Temkin adsorption isotherm also supports the adsorption phenomenon. These isotherms could infer that the plant extracts such as leaf sheath and staminate flower are found to be adsorbed on the MS surface and it could form a monolayer of adsorption.

Mechanism of inhibition using leaf sheath extract

From the literature survey it was found that the major phytochemical constituents present in L.S.E. are

- Cellulose
- Lignin

These phytochemical constituents have active adsorption centres. Greater the number of active centres stronger is the adsorption on MS surface. These constituents are being adsorbed on the MS surface and it forms a protective layer on MS. This layer prevents the metal dissolution and hydrogen evolution, thus retards corrosion. Numerous OH groups around the molecules present in the phytochemical constituent make them more ready to form strong links with hydrogen. In addition they can form complexes with metallic cations as Cu, Ca, Al, Fe, which are rarely soluble in aqueous environment. Probable iron – lignate complexes have been suggested (Sola 1978). These complexes can cause blocking of micro anodes and/or micro cathodes that are generated on the metal surfaces when in contact with electrolytes and so can retard the subsequent dissolution of the metal.



Molecular structure of lignin monomers

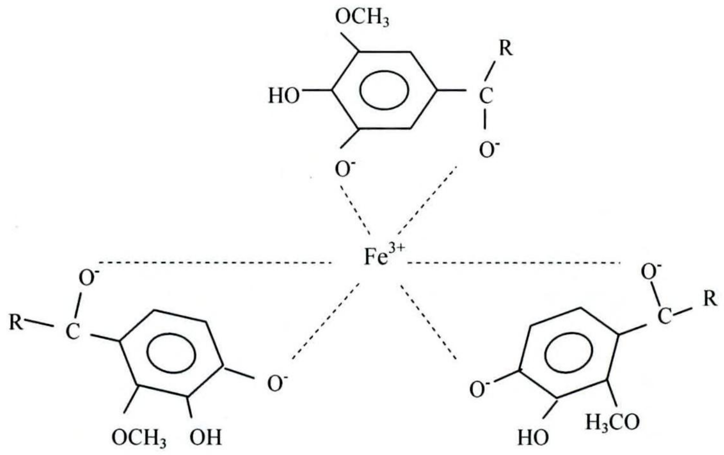


Fig-30

Part of the suggested structure for the ferric - lignate chelate where R represents the rest of the lignin molecule

Three lignate ions reacted with each ferric ion to form a stable octahedral co-ordination compound (fig-30). As lignin molecules are generally polymers of the basic flavanoid structure, each molecule could react with a number of ferric ions to form a network structure [Ross T.K. et al., 1978]. In the present investigation, it may be concluded that there was a formation of ferric – lignate complex on MS surface and that will form a protective blanketing layer on MS surface and prevent corrosion.

Mechanism of inhibition by staminate flower extract

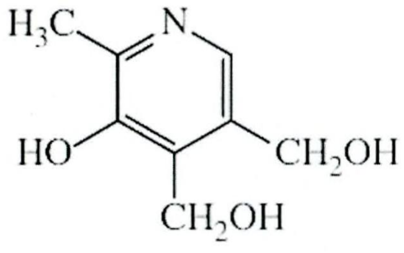
From the literature survey the phytochemical constituents present in Staminate flower extract of coconut are found to be

1. **Steroids:** a) Progesterone b) Hydroxy progesterone caproate

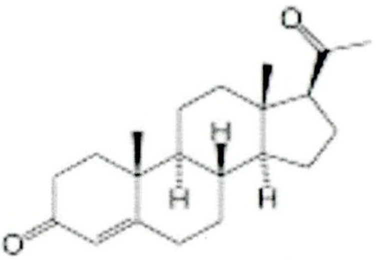
2. **Cations: a**) Sodium b) Ammonium c) Magnesium d) Calcium e) Iron f) Zinc

3. **Anions: a**) Chloride b) Phosphate c) Sulphate

4. **Acetate: a**) Lauric Acid b) Capric Acid c) Vitamin B6



Vit-B6/pyridoxine



Progesterone

These constituents of the extract are mostly composed of oxygen and nitrogen containing compounds. Adsorption of these compounds may also form complexes with metallic cations. In the present case the oxygen containing constituents of the extract and hydroxy aromatic compounds can form a complex layer on the metal surface.

The extract in HCl medium is believed to interact physically and chemically with the metal surface forming a protective layer and hence can retard the dissolution of the metal. Similar findings are furnished by Pravin Kar et al., (1993). The presence of cations such as Na, NH_4, Mg, Ca, Zn etc. and anions such as Cl^-, phosphate and sulphate might influence the inhibition through synergism.

Thus, the extract of staminate flower and leaf sheath are found to be promising inhibitors to retard the corrosion of MS in acid medium.