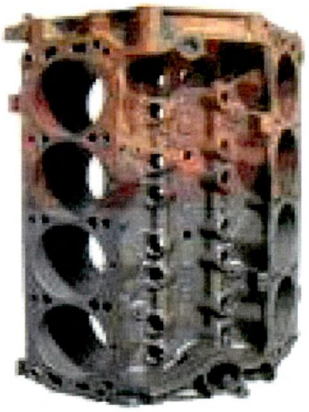


RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

Mild steel suffer from severe corrosion when it comes in contact with various acid solutions during the transportation of acid, descaling, storage of acids and other chemical processes. HCl and H_2SO_4 are frequently used for these purposes.

The use of an inhibitor during industrial processes such as acid cleaning, pickling, descaling, etching, etc is a better way to protect metals against corrosion. Inhibitors are often easy to apply and offer the advantage of *in situ* application without causing any significant disruption to the process. The use of chemical inhibitors has been limited because of the environmental threat. Plant extracts have become an alternative since they are environmentally acceptable, readily available and renewable source.

The corrosion inhibition performance of the acid extract of *Cassia fistula* leaves (CFL), *Bougainvillea spectabilis* leaves (BSL) and *Mirabilis jalapa* flowers (MJF), the stability of the extracts, the nature of inhibitor action in 1M HCl and 0.5M H_2SO_4 have been studied and the results obtained in the study are discussed in this chapter. The environmental impact of the selected plant extracts was analysed by bioaccumulation.

4.1 Weight loss measurements

4.1.1. Mild steel in 1M HCl

The percentage inhibition efficiency obtained from weight loss measurements at different concentrations of the CFL, BSL and MJF extracts and various immersion times in 1M HCl are summarized in tables 4.1 to 4.3. The effect of the extracts with respect to different parameters is discussed below.

Effect of Inhibitor concentration

The inhibition efficiency of various concentrations of the extracts of CFL, BSL and MJF for the dissolution of mild steel in 1M HCl is obtained from weight loss measurements and presented in the tables 4.1, 4.2 and 4.3 respectively.

Table 4.1

Variation of inhibition efficiency for mild steel corrosion in 1M HCl in the presence of various concentrations of CFL extract and immersion periods

Conc of the extract (%v/v)	Immersion period(in hours) / Percentage inhibition efficiency						
	1	3	5	7	12	24	48
0.05	31.44	38.53	69.22	83.03	82.80	47.31	19.30
0.50	47.39	64.11	82.08	87.91	94.99	79.14	34.77
1.00	59.99	76.29	86.03	90.62	95.58	79.47	40.32
2.00	68.29	81.70	89.61	91.12	96.43	89.42	52.75
3.00	70.41	82.79	90.68	92.97	97.00	93.63	58.01
4.00	74.97	84.94	91.33	94.27	97.44	94.62	61.77
5.00	77.56	86.81	92.03	94.51	97.50	95.21	64.34

Table 4.2

Variation of inhibition efficiency for mild steel corrosion in 1M HCl in the presence of various concentrations of BSL extract and immersion periods

Conc of the extract (%v/v)	Immersion period(in hours) / Percentage inhibition efficiency						
	1	3	5	7	12	24	48
0.05	18.43	29.04	31.49	41.43	66.30	83.27	84.25
0.50	24.77	31.72	56.53	58.41	74.42	89.56	95.94
1.00	29.62	35.32	61.94	61.20	81.87	90.00	95.63
2.00	34.36	40.95	61.30	68.80	82.97	91.86	96.18
3.00	48.45	49.90	62.51	81.35	84.62	92.37	96.55
4.00	51.90	57.73	68.84	82.71	85.78	92.98	96.14
5.00	55.59	60.57	72.41	83.25	87.64	93.88	96.14

Table 4.3

Variation of inhibition efficiency for mild steel corrosion in 1M HCl in the presence of various concentrations of MJF extract and immersion periods

Conc of the extract (%v/v)	Immersion period(in hours) / Percentage inhibition efficiency						
	1	3	5	7	12	24	48
0.05	42.49	45.19	45.21	45.28	81.28	89.91	33.23
0.50	58.09	58.70	62.16	63.11	89.34	93.76	66.62
1.00	59.66	61.50	69.73	72.73	90.46	95.94	68.82
2.00	62.11	64.53	73.00	77.35	91.83	96.66	73.05
3.00	68.39	71.35	77.82	79.02	93.46	96.62	76.84
4.00	73.11	75.78	78.78	83.02	94.47	97.54	76.22
5.00	75.21	76.52	79.80	83.27	95.17	97.81	76.06

From table 4.1 it is evident that the inhibition efficiency increased with increase in concentration of CFL. The maximum efficiency (97.5%) is obtained at 5 % v/v. Analysing the table thoroughly it seems that the inhibition efficiency does not vary much from 3% to 5% v/v (97-97.5%).

Inspection of table 4.2 reveals that the inhibition efficiency of BSL increases with increase in concentration and reached a maximum of 96.55% at 3% v/v concentration of the extract and it is almost constant above this concentration at longer immersion periods.

It is noted from table 4.3 that the percentage inhibition efficiency improved with increase in the concentration of the MJF extract. The maximum efficiency of 97.81% is obtained at 5% v/v concentration.

It has been found that the inhibition efficiency increases with increase in concentration of all the extracts for mild steel dissolution in 1M HCl. This behaviour may be attributed to the increase in the surface area covered by the adsorbed molecules of the inhibitor with increase in concentration.

The increase in inhibitive action with increase in concentration of the extract can also be ascribed to the increase in blocking of active sites of the mild steel surface. The active polar sites of the inhibitor molecules form a monolayer on the surface of the mild steel. (**Violet Dhayabaran *et al.*, 2003).**

The excellent inhibition efficiency (96.55 – 98.06%) may be attributed to the formation of a barrier layer due to the adsorption of the phytochemical constituents on the metal surface.

Effect of Immersion time

The variation of inhibition efficiency of CFL with immersion period is given in table 4.1. It is seen that the inhibition efficiency increased with immersion time and attained a maximum at 12 h and thereafter decreased. An excellent inhibition efficiency of 97.5% is obtained at 12 h.

The efficiency of BSL in 1M HCl increases with immersion time in the studied range of immersion periods, ie., from 1 h to 48 h (table 4.2) and provided a maximum efficiency of 96% at 3, 4 and 5% v/v of the extract at 48 h. At 24 h and 48 h, it is noted that even very low concentration (0.5% v/v) of the extract shows good efficiency. This may be due to the increase in surface coverage by the adsorption of the components present in the extract leading to strong adsorption.

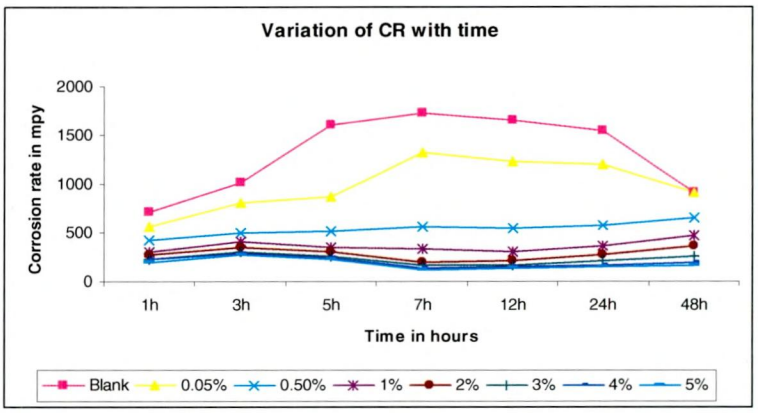
The IE of MJF in 1M HCl is given in table 4.3 which shows that IE increases with increase in immersion period. The maximum efficiency is obtained at 24 h after which the efficiency decreased at 48 h. At 12 h and 24 h, the IE values of MJF in 1M HCl did not show much difference and so it can be interpreted that the effective immersion time is 12 h. This shows the persistence of the adsorbed molecules of the extract on the mild steel surface over a longer test period.

The results show that all the three extracts act as good inhibitors in 1M HCl. The increase in inhibition efficiency with the period of immersion may be due to the increase in adsorption of phytoconstituents of the extract on the surface of mild steel.

The corrosion rate of mild steel in the absence and in the presence of various concentrations of the extracts has been calculated from weight loss measurements at different immersion periods and is represented in the figure 4.1 for BSL extract. It is noticed that the addition of the extract reduced corrosion rate effectively at all immersion periods.

Figure 4.1

Variation of corrosion rate for mild steel in 1M HCl in the absence and presence of various concentrations of BSL extract with immersion periods



The decrease in corrosion rate may be attributed to the adsorption of the phytochemical constituents present in the inhibitors on the mild steel surface. The adsorbed layer of the extract molecules, isolate the mild steel surface from the aggressive medium leading to the decrease in the corrosion rate.

4.1.2. Mild steel in 0.5M H_2SO_4

The percentage inhibition efficiency obtained from weight loss measurements at different concentrations of the CFL, BSL and MJF extracts and at various immersion times in 0.5M H_2SO_4 are summarized in tables 4.4 to 4.6.

Table 4.4

Variation of inhibition efficiency for mild steel corrosion in 0.5M H_2SO_4 in the presence of various concentrations of CFL extract and immersion periods

Conc of the extract (%v/v)	Immersion period(in hours) / Percentage inhibition efficiency						
	1	3	5	7	12	24	48
0.05	12.48	65.93	33.48	28.47	26.23	5.57	5.44
0.50	16.93	76.73	76.44	73.71	50.04	36.87	34.32
1.00	17.76	79.73	81.12	82.75	70.99	49.57	36.24
2.00	21.67	84.58	85.53	87.50	73.45	61.34	45.58
3.00	32.78	86.44	88.07	87.37	79.76	67.40	53.28
4.00	33.79	86.69	89.16	88.42	81.63	70.34	54.25
5.00	34.41	87.53	90.25	90.19	84.39	73.48	59.78

Table 4.5

Variation of inhibition efficiency for mild steel corrosion in 0.5M H_2SO_4 in the presence of various concentrations of BSL extract and immersion periods

Conc of the extract (%v/v)	Immersion period(in hours) / Percentage inhibition efficiency						
	1	3	5	7	12	24	48
0.05	20.85	21.45	45.29	23.65	25.36	22.16	5.62
0.50	40.22	50.53	67.43	67.51	66.84	62.68	28.49
1.00	58.70	60.33	77.94	81.08	81.39	76.95	48.28
2.00	61.77	65.64	80.82	88.19	87.13	82.04	60.64
3.00	67.52	69.69	84.03	90.77	90.02	86.18	70.94
4.00	69.15	71.82	84.92	92.47	91.17	89.40	78.88
5.00	73.03	73.10	85.63	93.00	91.74	90.22	82.09

Table 4.6

Variation of inhibition efficiency for mild steel corrosion in 0.5M H_2SO_4 in the presence of various concentrations of MJF extract and immersion periods

Conc of the extract (%v/v)	Immersion period(in hours) / Percentage inhibition efficiency						
	1	3	5	7	12	24	48
0.05	28.92	38.45	38.16	30.67	37.02	19.00	0.08
0.50	60.65	63.35	74.06	76.67	66.19	64.45	24.98
1.00	69.00	72.82	81.18	82.40	71.93	72.71	45.29
2.00	71.78	79.90	84.74	85.27	82.52	81.28	61.47
3.00	75.45	82.39	85.74	87.74	86.15	87.31	69.29
4.00	77.57	83.46	87.30	88.14	87.76	88.81	77.64
5.00	78.91	83.56	88.03	88.46	88.07	90.07	83.08

Effect of Inhibitor concentration

It has been found that all the extracts (CFL, BSL and MJF) inhibit the corrosion of mild steel in 0.5M H_2SO_4 at all concentrations used in the study. It has also been observed that the inhibition efficiency for all these extracts increased with increase in concentration which suggests that the inhibition process is sensitive to the amount of additive present.

From table 4.4 it is seen that the CFL extract in 0.5M H_2SO_4 showed a maximum efficiency of 90.25% at 5% v/v concentration. The increase in IE shows that the adsorption of the phytochemical constituents takes place with increase in concentration of the extract. The increase in efficiency with the increase in concentration of the extract is due to the increase in the surface area covered by the molecules of the extract.

The values in table 4.5 reveals that BSL provides a maximum efficiency at 5%v/v, but the variation is very less above 2%v/v concentration. The maximum efficiency obtained is 93% at 5%v/v concentration at 7h immersion period. From the inhibition efficiency values it is known that BSL acts as an effective inhibitor for the mild steel corrosion in 0.5M H_2SO_4.

It is observed from table 4.6 that the increase in concentration of the MJF extract leads to an increase in efficiency. A maximum of 90.07% efficiency is obtained at 5%v/v concentration of the inhibitor.

Organic compounds present in the extract can easily be adsorbed on mild steel and this gives rise to an increase in efficiency. As concentration of the extract increases, the molecules of the extract occupy more surface area on the mild steel and reduce the dissolution of the material in the acid medium.

Effect of immersion period

From the IE values given in table 4.4, it is noted that the IE of CFL increases with immersion period up to 5 h for all the concentrations except for 0.05% CFL where there is a sharp decrease from 3 h to 5 h (65% - 33%). This may be due to the insufficient concentration of the extract to cover the entire surface of the specimen thereby accelerating the corrosion on the uncovered surface. After 5 h, even though there is a decrease in IE with immersion period, the decrease is not significant at higher concentration of the extract up to 7 h period. After 7 h there is a steady decrease in IE with immersion period.

The optimum immersion period for the maximum efficiency for the dissolution of mild steel in 0.5M H_2SO_4 in the presence of BSL was found to be 7 h which is evident from table 4.5. Further increase in immersion period decreased the inhibition efficiency of the extract. This may be due to the desorption of the inhibitor, which may be a slow process, since the protection efficiency has not changed significantly till 24 h.

The inhibition efficiency of MJF in 0.5M H_2SO_4 at different immersion periods is given in table 4.6. From the table, it is noted that the efficiency increases with immersion time and reaches a maximum at 12 h after which it decreases. At higher concentrations from 2% v/v to 5%v/v, it is noted that there is no significant change in IE from 3h to 24h.

The variation of corrosion rate for the dissolution of mild steel in 0.5M H_2SO_4 for different immersion periods for the CFL and MJF extracts are represented in

figures 4.2 and 4.3 respectively. It is noticed that the corrosion rate in each immersion period decreased with increase in the inhibitor concentration.

Figure 4.2

Variation of corrosion rate for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of CFL extract with immersion period

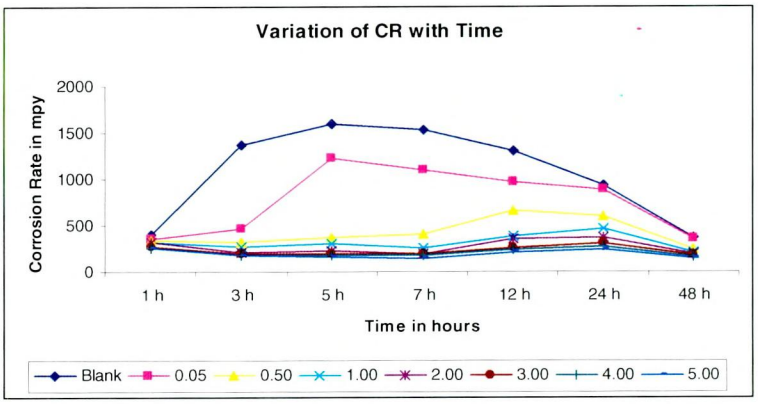
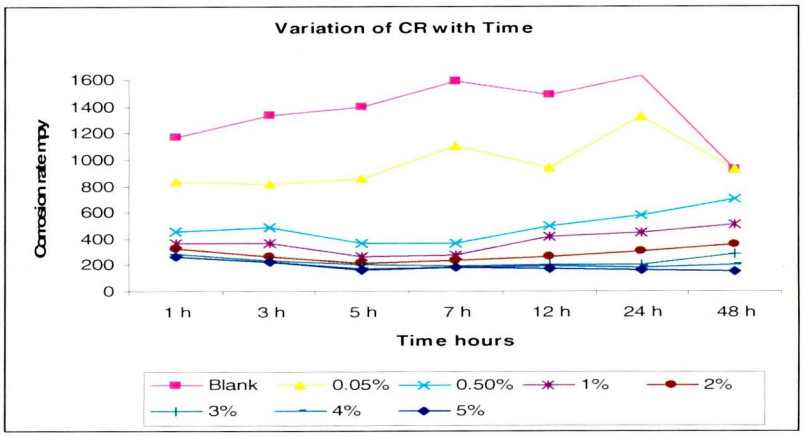


Figure 4.3

Variation of corrosion rate for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of MJF extract with immersion period



From the figures 4.2 and 4.3, it is evident that the corrosion rate has reduced when the concentration of the inhibitor is increased. There is a similar observation for BSL also.

The corrosion rate decreasing with immersion time may be ascribed to the adsorption of the corrosion product and the adsorption layer becoming thicker with immersion time which prevents corrosion of mild steel from the acid medium (**Xianghong Li *et al.*, 2009**).

4.2 Temperature study

Temperature has a greater impact on the rate of metal dissolution. Temperature effect on acidic corrosion, most often in hydrochloric and sulphuric acid have been the object of large number of investigations. Corrosion rate approximately doubles for every 10°C rise in temperature for corrosion accompanied by hydrogen gas evolution as in normal chemical reactions.

Acid pickling of steel is usually carried out at elevated temperatures upto 60^0C in HCl and upto 90^0C in sulphuric acid (**Popova *et al.*, 2003**). The chemically stable inhibitors are expected to provide high protection efficiency under these conditions. This is considered in the practical aspects of the present investigation. To evaluate the effect of temperature on the inhibition efficiency of CFL, BSL and MJF for the mild steel corrosion in 1M HCl, the study was carried out at 303, 313, 323, 333 and 343K for an immersion period of 1h.

The results of the experimental study on the effect of temperature on mild steel corrosion in 1M HCl in the presence of various concentrations of the extracts CFL, BSL and MJF are given in the tables 4.7, 4.8 and 4.9.

Table 4.7

Variation of inhibition efficiency for mild steel corrosion in 1M HCl in the presence of various concentrations of CFL extract with temperature

Conc of the extract (%v/v)	**Immersion Temperature in Kelvin/ Percentage inhibition efficiency**				
	303	**313**	**323**	**333**	**343**
0.05	31.44	14.77	39.02	20.49	26.75
0.50	47.39	53.72	66.51	60.20	57.50
1.00	59.99	69.20	75.59	63.10	71.12
2.00	68.29	77.07	86.43	83.34	83.01
3.00	70.41	79.77	86.71	87.03	87.56
4.00	74.97	83.59	90.16	88.46	91.80
5.00	77.56	85.93	91.01	93.06	93.40

Table 4.8

Variation of inhibition efficiency for mild steel corrosion in 1M HCl in the presence of various concentrations of BSL extract with temperature

Conc of the extract (%v/v)	Immersion Temperature in Kelvin/ Percentage inhibition efficiency				
	303	313	323	333	343
0.05	18.43	37.27	23.77	49.34	35.95
0.50	24.77	56.25	50.60	78.34	64.26
1.00	29.62	57.72	57.29	83.92	74.22
2.00	34.36	63.45	62.37	88.52	83.33
3.00	48.45	66.95	63.87	89.84	84.68
4.00	51.90	68.60	67.04	90.21	86.32
5.00	55.59	74.30	69.00	90.90	87.76

Table 4.9

Variation of inhibition efficiency for mild steel corrosion in 1M HCl in the presence of various concentrations of MJF extract with temperature

Conc of the extract (%v/v)	Immersion Temperature in Kelvin/ Percentage inhibition efficiency				
	303	313	323	333	343
0.05	42.49	52.77	60.84	51.85	16.58
0.50	58.09	68.68	79.73	75.45	40.65
1.00	59.66	73.70	85.11	82.01	62.14
2.00	62.11	74.75	85.45	85.36	63.95
3.00	68.39	80.40	87.61	87.82	71.39
4.00	73.11	82.78	88.90	89.46	75.45
5.00	75.21	84.58	91.43	90.73	81.44

From table 4.7, it is noted that the change in IE at lower concentration of the CFL extract, has no regular trend with change in temperature. At higher

concentrations the inhibition efficiency of the inhibitor increases with temperature. The increase in inhibition efficiency with temperature may be due to the specific interaction between the iron surface and the extract (**Ammer and Khorafi, 1973**). The efficiency does not increase significantly after 323 K. The maximum efficiency obtained is 93.4% at 343 K with 5%v/v concentrations of the extract. This suggests that the phytoconstituents of CFL adsorb strongly on the mild steel surface forming a protective layer on the mild steel surface.

An irregularity in the values of IE is noted from table 4.8. This may be due to the competition between dissolution of mild steel and partial desorption of the inhibitor from the metal surface with changes in temperature. At 5% v/v concentration of the extract, a maximum efficiency of 90.9% is obtained at 333 K. At each temperature, the IE increased with increase in concentration of the extract.

The IE of MJF in 1M HCl at different temperatures is given in table 4.9. The IE increased with increase in temperature till 323 K and then decreased with further increase in temperature. The decrease in efficiency at 333K and 343K may be due to desorption of the molecules of the extract from the surface of mild steel after adsorption till 323 K. At each temperature the efficiency increased with increase in concentration of the extract. The optimum temperature is found to be 323K. The maximum efficiency obtained is 91.43%.

The increase in inhibition efficiency with increase in temperature in case of CFL and MJF indicates that the adsorption phenomenon becomes more pronounced with increase of temperature. **Ivanov (1986)** states that increase in protection efficiency with increase in temperature is due to the change in the nature of the adsorption; the inhibitor is adsorbed physically at lower temperature, while chemisorption is favoured as temperature increases.

The variation of corrosion rate for mild steel in 1M HCl in the absence and in the presence of CFL and BSL extracts with temperature at 1 hour immersion period is shown in figures 4.4 and 4.5 respectively.

Figure 4.4

Variation of corrosion rate for mild steel in 1M HCl in the absence and in the presence of CFL extract with temperature

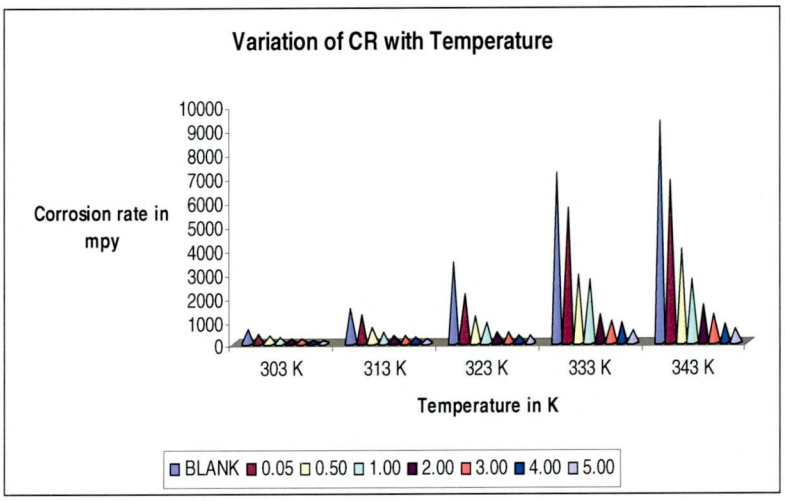
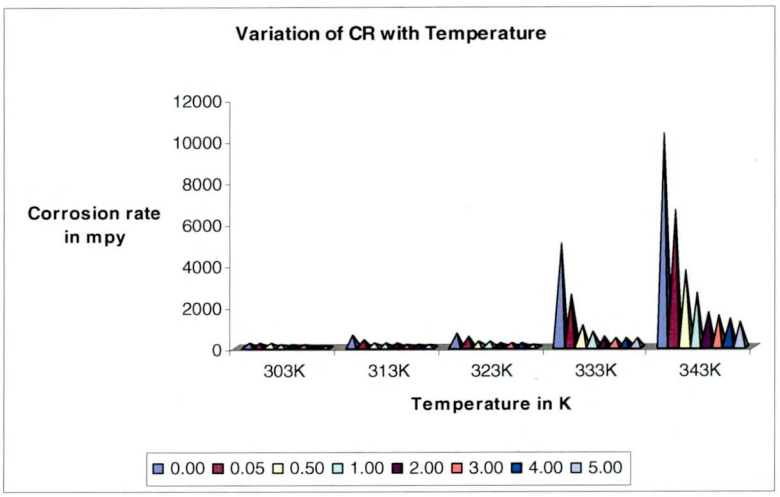


Figure 4.5

Variation of corrosion rate for mild steel in 1M HCl in the absence and in the presence of BSL extract with temperature



Inspecting the figures 4.4 and 4.5, it is noted that the corrosion rate increased with temperature as in other chemical reactions. The corrosion rate has considerably decreased with increase in the concentration of the extract at all temperatures studied. The decrease in CR with concentration is not obviously seen at lower temperatures, whereas at higher temperatures ie) at 323 K to 343 K the decrease in CR with concentration is obvious. At all the temperatures the corrosion rate showed a minimum decrease after 2% v/v of all the extracts in 1M HCl.

The results of the experimental study on the effect of temperature on mild steel corrosion in 0.5M H_2SO_4 in the presence of various concentrations of CFL, BSL and MJF extract are given in the tables 4.10, 4.11 and 4.12 respectively.

Table 4.10

Variation of inhibition efficiency for mild steel corrosion in 0.5M H_2SO_4 in the presence of different concentrations of CFL extract with temperature

Conc of the extract (%v/v)	Immersion Temperature in Kelvin/ Percentage inhibition efficiency				
	303	313	323	333	343
0.05	12.48	15.33	25.43	19.00	16.05
0.50	16.93	61.11	65.86	49.14	38.15
1.00	17.76	68.54	70.41	65.18	45.98
2.00	21.67	74.13	75.99	70.73	57.74
3.00	32.78	76.75	78.08	75.61	62.32
4.00	33.79	79.37	79.06	76.43	64.73
5.00	34.41	80.93	83.01	77.34	70.65

Table 4.11

Variation of inhibition efficiency for mild steel corrosion in 0.5M H_2SO_4 in the presence of different concentrations of BSL extract with temperature

Conc of the extract (%v/v)	Immersion Temperature in Kelvin/ Percentage inhibition efficiency				
	303	313	323	333	343
0.05	20.85	20.93	32.47	21.02	17.34
0.50	40.22	65.01	62.42	54.32	44.00
1.00	58.70	75.20	73.35	73.48	54.66
2.00	61.77	79.67	81.80	81.34	67.12
3.00	67.52	83.14	84.48	85.32	75.68
4.00	69.15	84.49	84.91	87.84	79.94
5.00	73.03	86.09	86.09	90.48	81.97

Table 4.12

Variation of inhibition efficiency for mild steel corrosion in 0.5M H_2SO_4 in the presence of different concentrations of MJF extract with temperature

Conc of the extract (%v/v)	Immersion Temperature in Kelvin/ Percentage inhibition efficiency				
	303	313	323	333	343
0.05	28.92	16.56	25.40	18.90	13.57
0.50	60.65	57.22	66.71	57.48	39.54
1.00	69.00	69.51	72.86	65.66	53.31
2.00	71.78	78.55	80.92	77.32	69.47
3.00	75.45	80.33	84.78	81.44	74.75
4.00	77.57	82.18	86.19	83.35	78.41
5.00	78.91	84.37	88.37	86.16	82.56

It is observed from table 4.10 that the efficiency of CFL increased with increase in temperature and reached a maximum at 323 K after which there is a decrease. The maximum efficiency is 83.01% for 5% v/v of CFL at 323 K. The increase in efficiency with increase in concentration is well significant at each studied temperature.

From the IE values given in table 4.11, it is evident that at higher concentrations ie., at and above 2%v/v the IE increased with temperature up to 333K after which there is a decrease in IE which may be due to the desorption of the inhibitor molecules from the mild steel surface. A maximum of 90.48% is obtained at 333 K for 5% v/v concentration of BSL. The BSL extract seems to be an effective inhibitor up to 333 K.

The IE values given in table 4.12 shows that at lower concentrations, there is no regular change in IE with temperature, however at and above 1% v/v concentration the efficiency increased with temperature up to 323 K and thereafter there is a decrease in IE. This decrease in efficiency may be due to desorption of the extract molecules from the mild steel surface. The maximum efficiency obtained with MJF in 0.5M H_2SO_4 is 88.37% at 323 K.

All the three extracts tested (CFL, BSL and MJF in 0.5M H_2SO_4) are found to be effective at elevated temperatures for higher concentrations of the extract.

The corrosion rates of mild steel in 0.5 M H_2SO_4 in absence and in the presence of various concentrations of the CFL, BSL and MJF extracts at different temperatures ranging from 303K to 343 K is shown in figures 4.6, 4.7 and 4.8 respectively.

Figure 4.6

Variation of corrosion rate for mild steel in 0.5M H_2SO_4 in the absence and in the presence of CFL extract with temperature

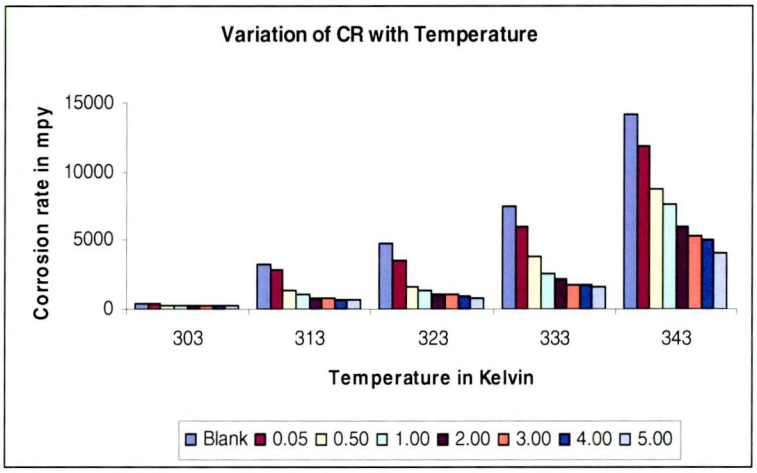


Figure 4.7

Variation of corrosion rate for mild steel in 0.5M H_2SO_4 in the absence and in the presence of BSL extract with temperature

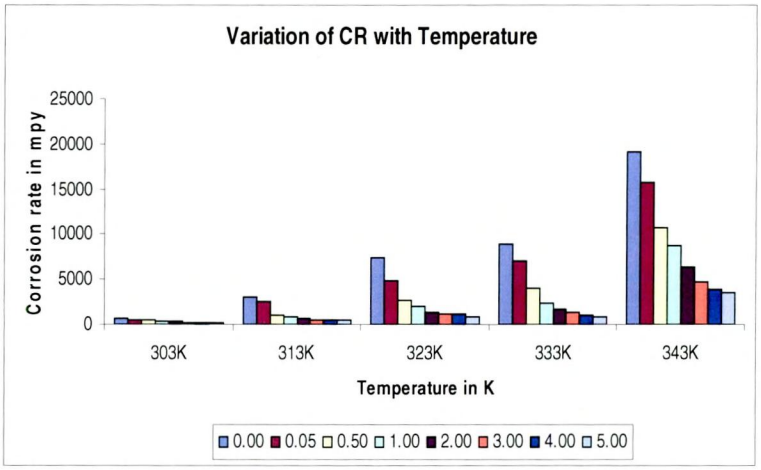
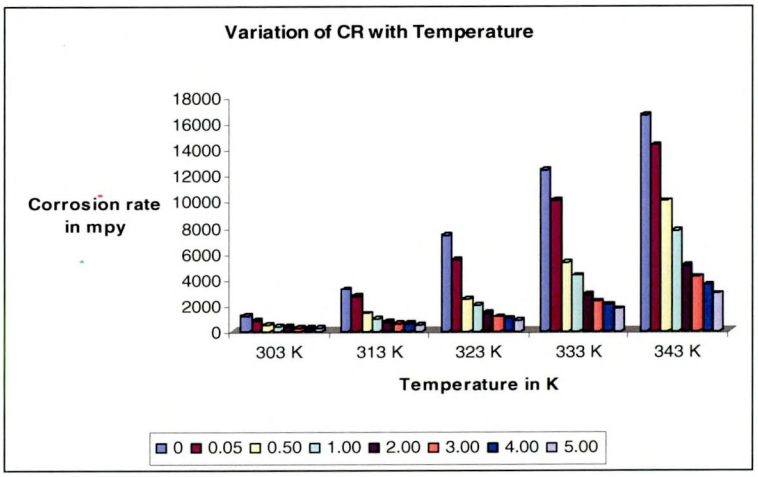


Figure 4.8

Variation of corrosion rate for mild steel in 0.5M H_2SO_4 in the absence and in the presence of MJF extract with temperature



From the figures 4.6, 4.7 and 4.8 it is noted that the corrosion rate increased with increase in temperature. It is seen that the corrosion rate at each temperature decreased with increase in the concentration of the extracts. At lower concentrations the decrease in corrosion rate is not so significant at any of the studied temperatures.

4.3 Adsorption Isotherms

Inhibitors protect metals from corrosion by adsorbing onto the surface by forming a thin adsorption layer. The efficiency of an inhibitor is largely dependent on the extent of adsorption of the inhibitor molecules on the metal surface. The nature of corrosion inhibitor has been deduced in terms of the adsorption characteristics of the inhibitor.

The establishment of isotherms that describe the adsorption behaviour of the inhibitor is important as they can provide important clues about the nature of metal-inhibitor interaction.

The adsorption characteristic of the extract is evaluated by plotting surface coverage against inhibitor concentration using the common adsorption isotherms namely Langmuir, Freundlich and Temkin isotherms.

All these isotherms are of the general form

$$f(\theta,x)\exp(-2a\,\theta)=kC$$

f(θ,x) is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm, θ is the surface coverage, C is the inhibitor concentration in the corroding medium, x, the size factor ratio, a is the molecular interaction parameter and k – the equilibrium constant of the adsorption process. The surface coverage was obtained from the weight loss measurements.

Four types of adsorption may take place by organic molecules at the metal/solution interface

1. Electrostatic attraction between the charged molecule and the charged metal
2. Interaction of uncharged electron pairs in the molecules with the metal
3. Interaction of π electrons with the metal and
4. Combination of 1 and 3 (**Paul Schweinsberg *et al.*, 1988)**

Langmuir Adsorption Isotherm

A correlation between θ, the surface coverage and concentration of inhibitor in the electrolyte can be represented by Langmuir adsorption isotherm (**Bentiss *et al.*, 1999).**

The plot of log θ/1-θ vs. log C for the dissolution of mild steel in 1M HCl in the absence and in the presence of various concentrations of CFL, BSL and MJF extracts at different temperatures is presented in figures 4.9, 4.10 and 4.11 respectively.

Figure 4.9

Langmuir adsorption isotherm for the mild steel dissolution in 1M HCl in the presence of various concentrations of CFL extract at different temperatures

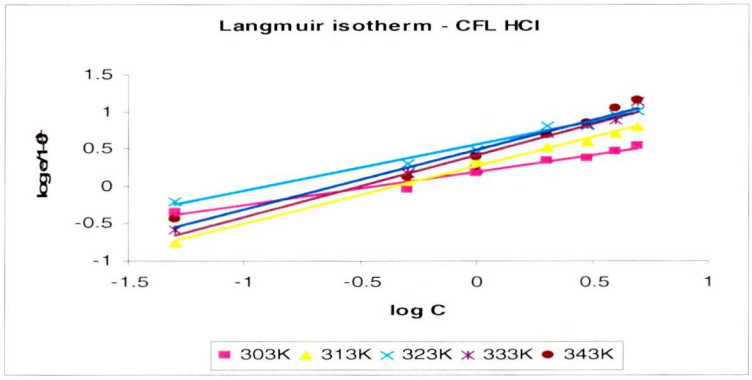


Figure 4.10

Langmuir adsorption isotherm for the mild steel dissolution in 1M HCl in the presence of various concentrations of BSL extract at different temperatures

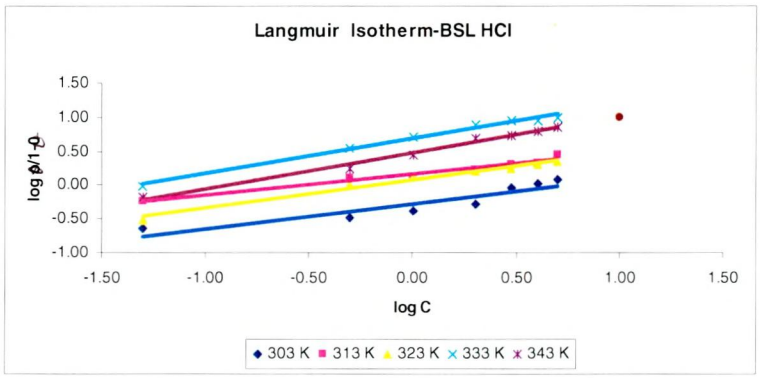
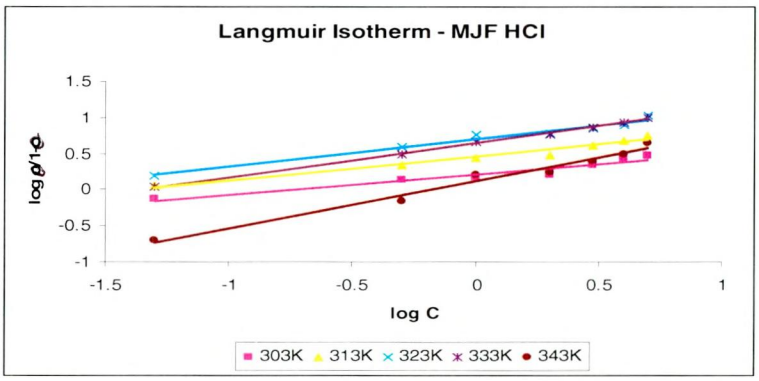


Figure 4.11

Langmuir adsorption isotherm for the mild steel dissolution in 1M HCl in the presence of various concentrations of MJF extract at different temperatures



The plots of log θ/1-θ vs log C were linear for all the extracts (CFL, BSL and MJF) at all the studied temperatures for the dissolution of mild steel in 1M HCl, showing that the adsorption follows Langmuir adsorption isotherm.

The linear regression analysis values of Langmuir adsorption isotherm for the dissolution of mild steel in 1M HCl for the CFL, BSL and MJF extracts at different temperatures are presented in table 4.13.

Table 4.13

Linear regression analysis of Langmuir Adsorption Isotherm for the dissolution of mild steel in 1M HCl in presence of the extracts at different temperatures

Extract	Temperature in K	Slope	Intercept	Correlation coefficient (R^2)
CFL	303	0.44	0.19	0.99
	313	0.76	0.27	1.00
	323	0.61	0.56	0.99
	333	0.83	0.42	0.99
	343	0.79	0.49	0.99
BSL	303	0.37	-0.27	0.92
	313	0.31	0.17	0.99
	323	0.42	0.08	0.99
	333	0.51	0.69	0.99
	343	0.53	0.48	0.99
MJF	303	0.29	0.22	0.97
	313	0.33	0.46	0.98
	323	0.39	0.70	0.99
	333	0.47	0.64	1.00
	343	0.65	0.12	0.99

The R^2 values greater than 0.9 in the regression analysis shows that the adsorption of the inhibitors in 1M HCl on the surface of mild steel follows Langmuir adsorption isotherm at all the studied temperatures.

The adsorption of the extract follows Langmuir isotherm with perfect linearity for CFL in 1M HCl at 313 K and MJF in 1M HCl at 333 K. As the adsorption follows Langmuir isotherm, it implies monolayer adsorption of CFL, BSL and MJF extracts on the mild steel surface.

Though the Langmuir plots are linear, the deviation of slopes from unity can be attributed to the molecular interaction among the adsorbed species.

The plots of log $\theta/1-\theta$ vs log C for the dissolution of mild steel in 0.5M H_2SO_4 in the presence of various concentrations of CFL, BSL and MJF extracts with temperature is given in figures 4.12, 4.13 and 4.14 respectively.

Figure 4.12

Langmuir adsorption isotherm for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of CFL extract at different temperatures

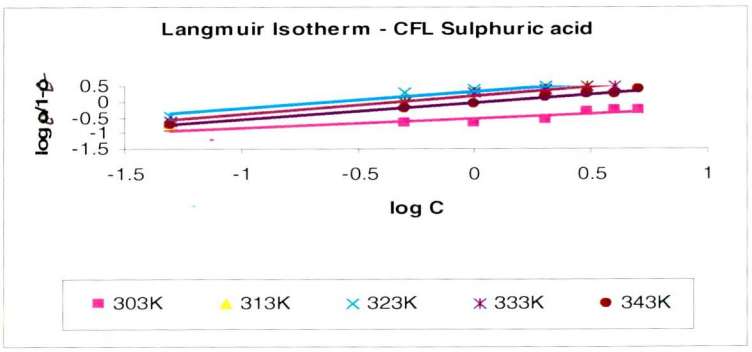


Figure 4.13

Langmuir adsorption isotherm for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of BSL extract at different temperatures

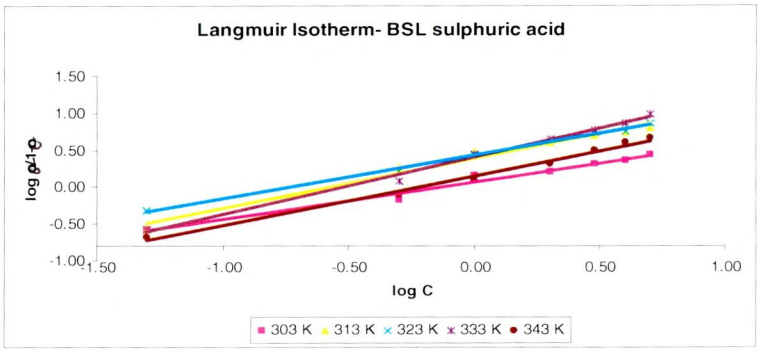
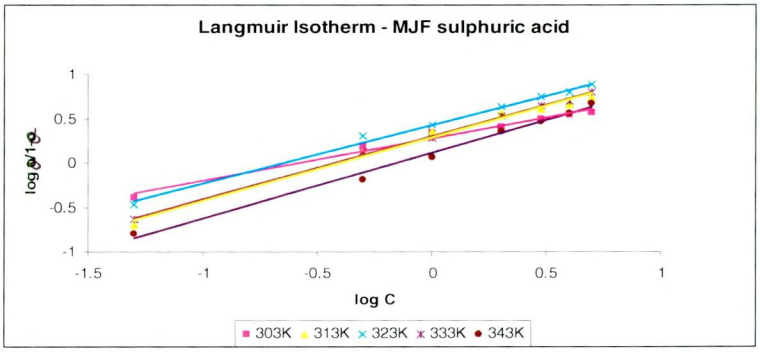


Figure 4.14

Langmuir adsorption isotherm for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of MJF extract at different temperatures



The mechanism of inhibition of corrosion is generally due to the formation and maintenance of a protective film on the metal surface (**Bhajiwala and Vashi, 2001**). The plot of log θ/1- θ against log C gave straight lines (Figures 4.12, 4.13 and 4.14) at all the temperatures for all the three extracts in 0.5M H_2SO_4 which suggests that the molecules cover both the anodic and cathodic regions through adsorption following Langmuir isotherm.

The linear regression analysis of the Langmuir plots for the dissolution of mild steel in 1M HCl in presence of CFL, BSL and MJF extracts at various temperatures are presented in table 4.14.

Table 4.14

Linear regression analysis of Langmuir Adsorption Isotherm for the dissolution of mild steel in 0.5M H_2SO_4 in presence of the extracts at different temperatures

Extract	Temperature in K	Slope	Intercept	Correlation coefficient(R^2)
CFL	303	0.30	-0.54	0.91
	313	0.66	0.23	0.97
	323	0.55	0.32	0.98
	333	0.60	0.18	0.99
	343	0.54	-0.04	1.00
BSL	303	0.51	0.07	0.99
	313	0.68	0.38	0.99
	323	0.59	0.44	1.00
	333	0.78	0.40	1.00
	343	0.67	0.15	0.99
MJF	303	0.47	0.27	0.99
	313	0.71	0.29	0.99
	323	0.66	0.43	1.00
	333	0.71	0.30	1.00
	343	0.74	0.11	1.00

The dissolution of mild steel in 0.5 M H_2SO_4 in the presence of CFL, BSL and MJF extracts obey Langmuir adsorption isotherm at all temperatures. This has been confirmed from the correlation coefficient values presented in table 4.14. The deviation of slope from unity is attributed to molecular interactions in the adsorbed layer which correspond to the observed physical adsorption mechanism. The value of slope increases at higher temperature indicating that the strength of attractive behavior of the inhibitor increases with temperature (**Ebenso *et al.*, 2009).**

Freundlich adsorption isotherm

The plot of log θ vs log C for the dissolution of mild steel in 1M HCl in the presence of various concentrations of CFL, BSL and MJF with temperature is shown in figures 4.15, 4.16 and 4.17 respectively.

Figure 4.15

Freundlich adsorption isotherm for the mild steel dissolution in 1M HCl in the presence of various concentrations of CFL extract at different temperatures

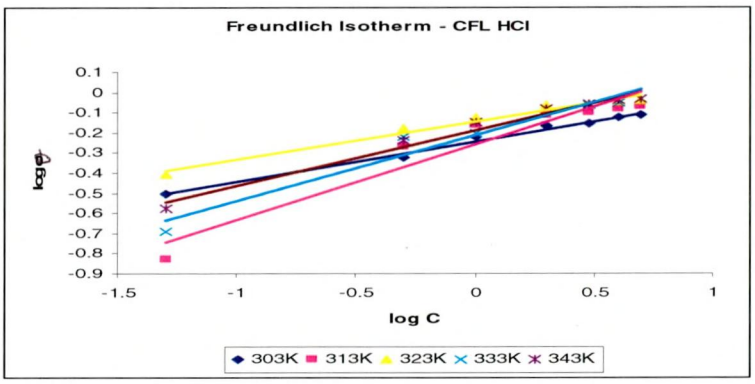


Figure 4.16

Freundlich adsorption isotherm for the mild steel dissolution in 1M HCl in the presence of various concentrations of BSL extract at different temperatures

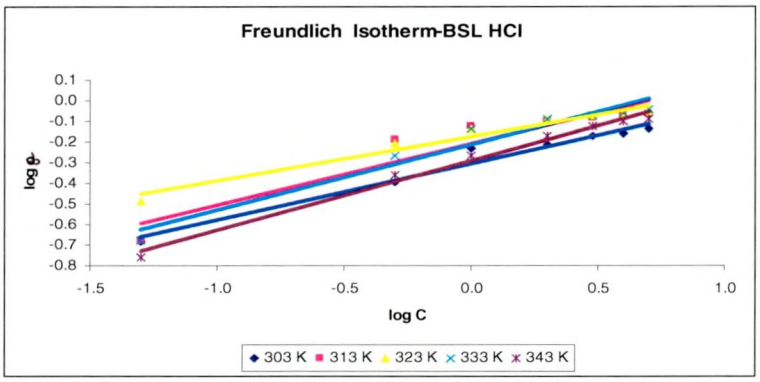
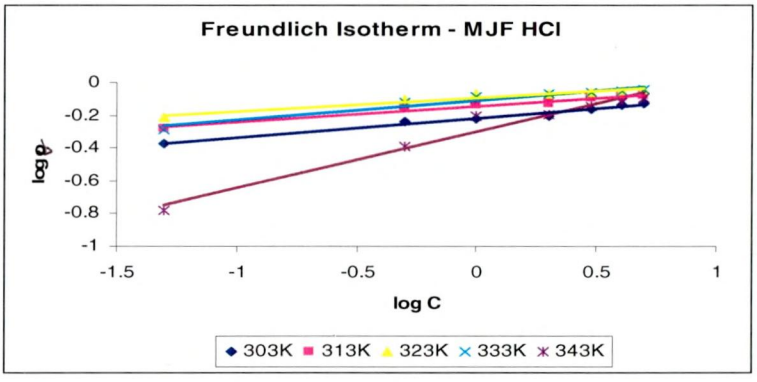


Figure 4.17

Freundlich adsorption isotherm for the mild steel dissolution in 1M HCl in the presence of various concentrations of MJF extract at different temperatures



The adsorption coefficient, slope and linear correlation coefficients from the regressions between log θ and log C are listed in table 4.15.

Table 4.15

Linear regression analysis of Freundlich Adsorption Isotherm for the dissolution of mild steel in 1M HCl in presence of the extracts at different temperatures

Extract	Temperature in K	Slope	Intercept	Correlation coefficient(R^2)
CFL	303	0.20	-0.24	0.99
	313	0.38	-0.26	0.96
	323	0.19	-0.14	0.99
	333	0.32	-0.21	0.98
	343	0.27	-0.19	0.99
BSL	303	0.25	-0.47	0.95
	313	0.14	-0.24	0.99
	323	0.23	-0.29	0.97
	333	0.13	-0.11	0.96
	343	0.17	-0.15	0.99
MJF	303	0.12	-0.22	0.99
	313	0.10	-0.14	0.99
	323	0.08	-0.09	0.97
	333	0.12	-0.11	0.98
	343	0.34	-0.30	0.98

Freundlich adsorption isotherms for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of CFL, BSL and MJF extract at different temperatures are given in figures 4.18, 4.19 and 4.20 respectively.

Figure 4.18

Freundlich adsorption isotherm for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of CFL extract at different temperatures

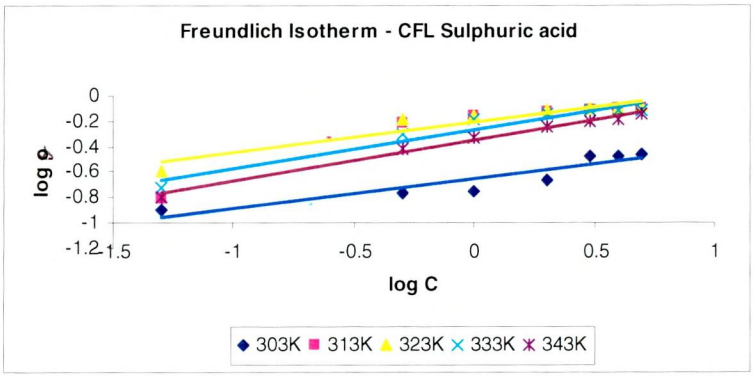


Figure 4.19

Freundlich adsorption isotherm for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of BSL extract at different temperatures

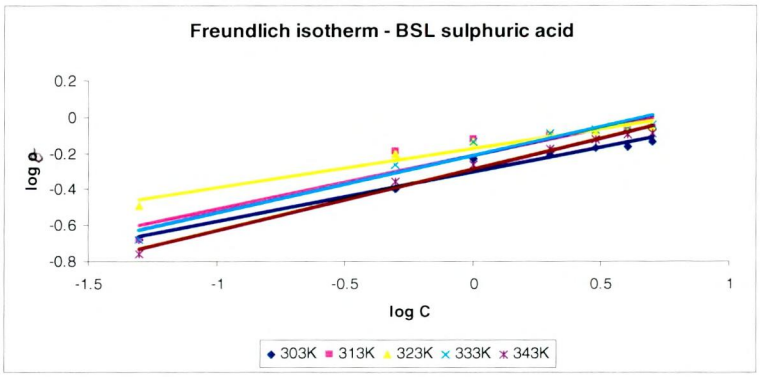
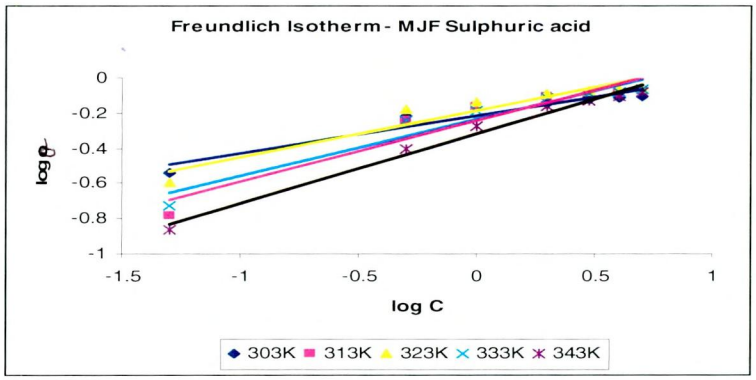


Figure 4.20

Freundlich adsorption isotherm for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of MJF extract at different temperatures



The slope, intercept and the regression values obtained from the Freundlich adsorption isotherms for the dissolution of mild steel in 0.5M H_2SO_4 are presented in table 4.16.

Table 4.16

Linear regression analysis of Freundlich Adsorption Isotherm for the dissolution of mild steel in 0.5M H_2SO_4 in presence of the extracts at different temperatures

Extract	Temperature in K	Slope	Intercept	Correlation coefficient(R^2)
CFL	303	0.23	-0.66	0.92
	313	0.35	-0.26	0.93
	323	0.24	-0.21	0.94
	333	0.31	-0.27	0.97
	343	0.32	-0.35	0.99
BSL	303	0.28	-0.30	0.98
	313	0.30	-0.21	0.94
	323	0.22	-0.17	0.98
	333	0.32	-0.21	0.97
	343	0.34	-0.29	0.99
MJF	303	0.21	-0.21	0.96
	313	0.35	-0.24	0.95
	323	0.26	-0.19	0.96
	333	0.32	-0.24	0.97
	343	0.40	-0.31	0.99

The adsorption of the extract molecules obeys Freundlich adsorption isotherm at all the studied temperatures in both 1M HCl and 0.5M H_2SO_4. This is confirmed from the correlation coefficient values given in tables 4.15 and 4.16.

Temkin Adsorption Isotherm

The applicability of Temkin's adsorption isotherm verifies the assumption of monolayer adsorption on a uniform, homogenous metal surface with an interaction in the adsorption layer.

The metal surface in aqueous solution is always covered with adsorbed water dipoles. The adsorption of inhibitor molecules takes place by the replacement of one or more water molecules from the surface of the metal. Therefore, adsorption of the inhibitor molecules on the surface of the metal is a quasi substitution process.

The adsorption of an organic molecule at a metal – solution interface can be represented as substitutional process between the organic molecules in the aqueous solution and the water molecules on the metallic surface H_2O_{ads} **(Moretti *et al.*, 1994).**

$$Org_{sol} + XH_2O_{ads} \rightarrow Org_{ads} + X\,H_2O_{sol}$$

where Org_{sol} and Org_{ads} are the organic molecules in the aqueous solution and adsorbed onto the metal surface respectively, H_2O_{ads} is the water molecules on the metallic surface, X is the size ratio representing the number of water molecules replaced by one molecule of the organic adsorbate.

The plots of θ vs log C for the mild steel dissolution in 1M HCl in the presence of CFL, BSL and MJF extracts are represented in the figures 4.21, 4.22 and 4.23 respectively.

Figure 4.21

Temkin adsorption isotherm for the mild steel dissolution in 1M HCl in the presence of various concentrations of CFL extract at different temperatures

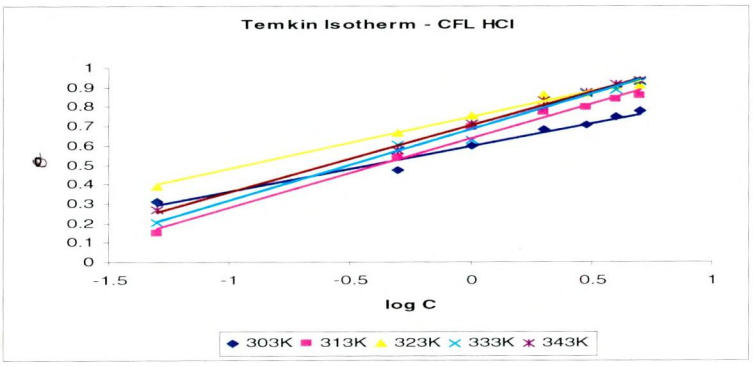


Figure 4.22

Temkin adsorption isotherm for the mild steel dissolution in 1M HCl in the presence of various concentrations of BSL extract at different temperatures

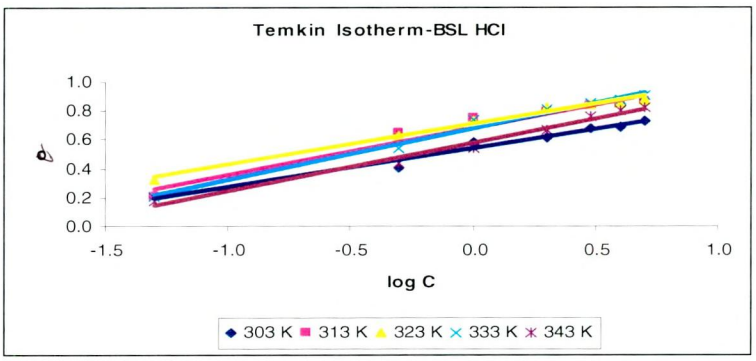
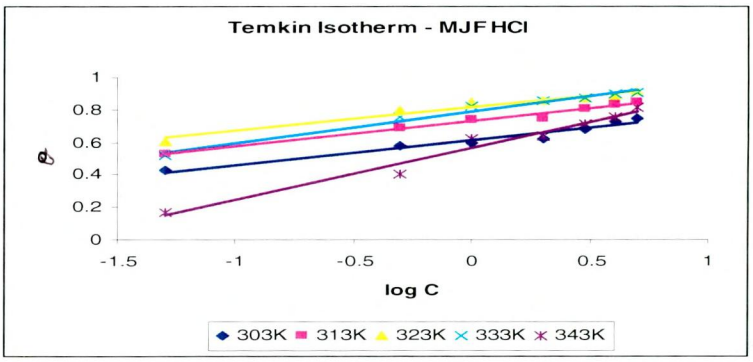


Figure 4.23

Temkin adsorption isotherm for the mild steel dissolution in 1M HCl in the presence of various concentrations of MJF extract at different temperatures



The adsorption parameters deduced from Temkin isotherm are presented in table 4.17.

Table 4.17

Linear regression analysis of Temkin Adsorption Isotherm for the dissolution of mild steel in 1M HCl in presence of the extracts at different temperatures

Extract	Temperature in K	Slope	Intercept	Correlation coefficient (R^2)	a	log k	ΔG kJ/mole
CFL	303	0.24	0.60	0.99	9.74	2.53	24.79
	313	0.36	0.64	0.99	6.43	1.78	21.34
	323	0.27	0.75	0.99	8.62	2.79	28.07
	333	0.36	0.68	0.99	6.32	1.88	23.08
	343	0.34	0.71	1.00	6.70	2.06	24.97
BSL	303	0.19	0.36	0.90	12.41	1.96	6.74
	313	0.17	0.59	0.99	13.47	3.48	13.52
	323	0.22	0.55	0.99	10.37	2.47	12.99
	333	0.21	0.80	0.97	11.09	3.86	21.34
	343	0.25	0.73	0.99	9.34	2.95	16.49
MJF	303	0.16	0.62	0.98	14.88	3.98	33.23
	313	0.16	0.73	0.99	14.88	4.71	35.05
	323	0.15	0.82	0.98	15.87	5.63	45.61
	333	0.19	0.79	0.99	11.95	4.1	37.29
	343	0.32	0.57	0.99	7.17	1.76	23.03

Adherence to the Temkin isotherm is an evidence of the adsorption of extract molecules on the mild steel surface from the acid medium. This is confirmed from the linear regression values presented in table 4.17.

The values of 'a' depend on the intermolecular interaction in the adsorption layer and on the heterogeneity of the surface. The positive values of 'a' shows the attractive force existing in the adsorbed layer. The higher values of 'a' shows a high degree of surface coverage and hence better inhibitive property of the extracts. K

denotes the strength between adsorbate and adsorbent. Larger values of k obtained imply that adsorption is more efficient and hence a better inhibition efficiency.

The low values of ΔG for the adsorption of BSL on mild steel may be due to excess free energy used for the adsorption of water molecules (**Odoemelam and Eddy, 2008).** ΔG values obtained from the Temkin isotherm for MJF at 303 to 333 K ranged from 33 kJ/mol to 46 kJ/mol which states that the adsorption tends to chemisorption at this temperature range (**Ramesh Saliyan and Vasudeva Adikary, 2008).**

The Temkin adsorption plots for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of CFL, BSL and MJF extracts at different temperatures are given in figures 4.24, 4.25 and 4.26 respectively.

Figure 4.24

Temkin adsorption isotherm for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of CFL extract at different temperatures

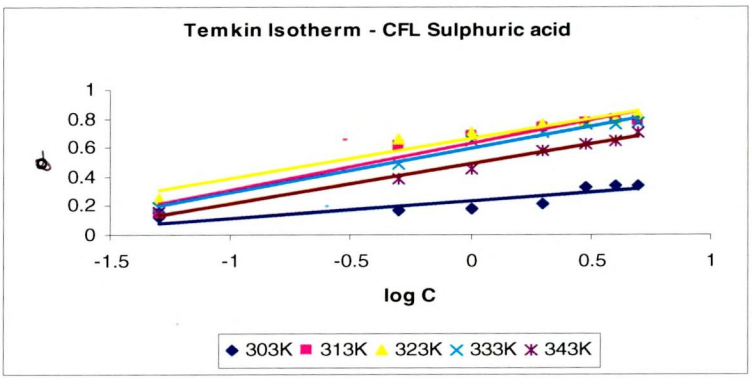


Figure 4.25

Temkin adsorption isotherm for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of BSL extract at different temperatures

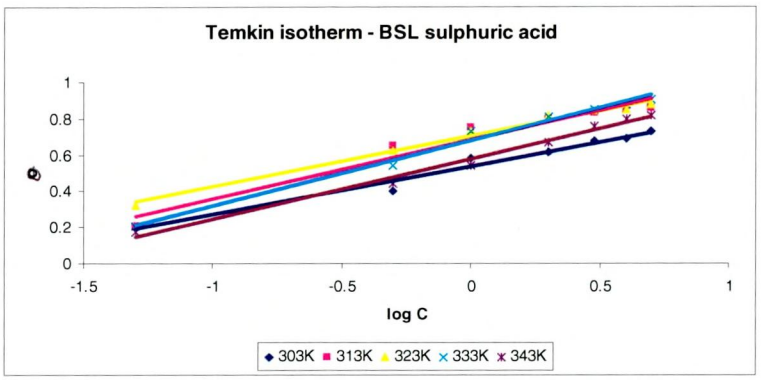
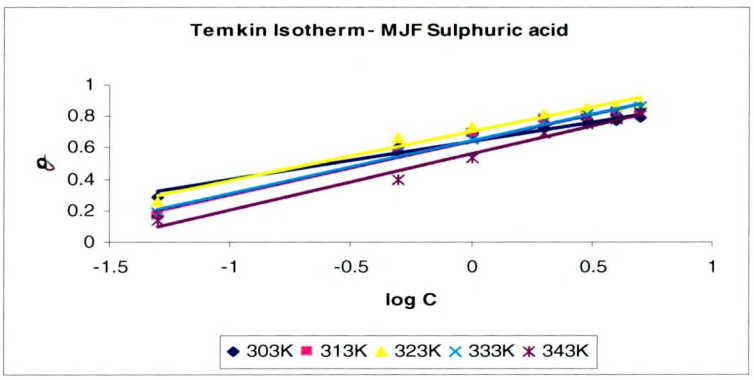


Figure 4.26

Temkin adsorption isotherm for the mild steel dissolution in 0.5M H_2SO_4 in the presence of various concentrations of MJF extract at different temperatures



Figures 4.24 -4.26 indicate that the plots of θ vs log C are linear, implying that the temkin adsorption isotherm is valid for the dissolution of mild steel in 0.5M H_2SO_4 in the presence of all the three extracts used. The results confirm that the corrosion inhibition of the extracts is attributed to the adsorption of the phytochemicals present in the extracts on the surface of mild steel.

The linear regression values and the values of molecular interaction parameter 'a' and equilibrium constant of adsorption K obtained from Temkin plots for the dissolution of mild steel in 0.5 M H_2SO_4 are given in table 4.18.

Table 4.18

Linear regression analysis of Temkin Adsorption Isotherm for the dissolution of mild steel in 0.5M H_2SO_4 in presence of the extracts at different temperatures

Extract	Temperature in K	Slope	Intercept	Correlation coefficient (R^2)	a	log k	ΔG kJ/mole
CFL	303	0.12	0.23	0.87	19.99	2.04	21.94
	313	0.32	0.63	0.97	7.26	1.98	22.30
	323	0.28	0.66	0.97	8.37	2.41	25.71
	333	0.30	0.60	0.99	7.61	1.98	23.73
	343	0.27	0.49	0.99	8.54	1.82	23.38
BSL	303	0.27	0.54	0.99	8.67	2.04	10.88
	313	0.32	0.68	0.98	7.14	2.12	13.83
	323	0.28	0.71	0.99	8.21	2.52	15.37
	333	0.36	0.68	0.99	6.47	1.91	14.42
	343	0.33	0.58	0.99	6.91	1.74	12.90
MJF	303	0.25	0.64	0.98	9.33	2.61	13.48
	313	0.34	0.65	0.99	6.75	1.89	12.86
	323	0.31	0.70	0.99	7.40	2.25	14.79
	333	0.34	0.65	1.00	6.82	1.92	13.85
	343	0.36	0.56	0.99	6.47	1.58	12.44

El-Awady thermodynamic model

As the slope values of Langmuir adsorption isotherm deviate from unity, the experimental data were fit into El-Awady's thermodynamic model to find the number of active sites (1/Y) occupied by the inhibitor molecules.

The results obtained from the El-Awady thermodynamic kinetic model for the dissolution of mild steel in 1M HCl and 0.5M H_2SO_4 are given in tables 4.19 and 4.20 respectively. El-Awady model is explained by the equation,

$$\log \theta/1-\theta = \log k + y \log C$$

from which 1/slope gives the number of active sites occupied by the inhibitor molecules and the intercept is log k, where k is the binding constant of the adsorption reaction.

Table 4.19

El Awady Thermodynamic model for the dissolution of mild steel in 1M HCl in presence of the extracts with temperature

Extract	Temperature in K	1/Y	log k
CFL	303	2	0.42
	313	1	0.36
	323	1	0.91
	333	1	0.51
	343	1	0.62
BSL	303	3	-0.71
	313	3	0.56
	323	2	0.19
	333	2	1.34
	343	2	0.91
MJF	303	3	0.75
	313	3	1.37
	323	3	1.82
	333	2	1.36
	343	2	0.18

Table 4.20

El Awady Thermodynamic model for the dissolution of mild steel in 0.5M H_2SO_4 in presence of the extracts with temperature

Extract	Temperature in K	1/Y	log k
CFL	303	3	-1.82
	313	2	0.35
	323	2	0.59
	333	2	0.30
	343	2	-0.07
BSL	303	2	0.13
	313	1	0.56
	323	2	0.74
	333	1	0.52
	343	1	0.22
MJF	303	2	0.58
	313	1	0.40
	323	2	0.65
	333	1	0.43
	343	1	0.15

1/Y ranges from 1 to 3 for all the three extracts at all the studied temperatures in both 1M HCl and 0.5M H_2SO_4. This shows that more than one water molecule is replaced from the mild steel surface by the phytoconstituents and these molecules get adsorbed on the corroding site of the mild steel thus producing an effective inhibition. Thus the number of active sites involved in corrosion is represented by the simple equation,

$Fe(H_2O)_x$ + inhibitor molecule → Fe $(inh)_x$ + xH_2O, where x ranges from 1 to 3.

4.4 Erying and Arrhenius plots for HCl medium

4.4.1 Erying plot for HCl medium

Erying plot is obtained by plotting log CR/T vs. 1/T. The Erying plots for the mild steel dissolution in 1M HCl in the absence and in the presence of the CFL, BSL and MJF extract are shown in the figures 4.27, 4.28 and 4.29 respectively.

Figure 4.27

Erying plot for the mild steel dissolution in 1M HCl in the absence and in the presence of various concentrations of CFL extract at different temperatures

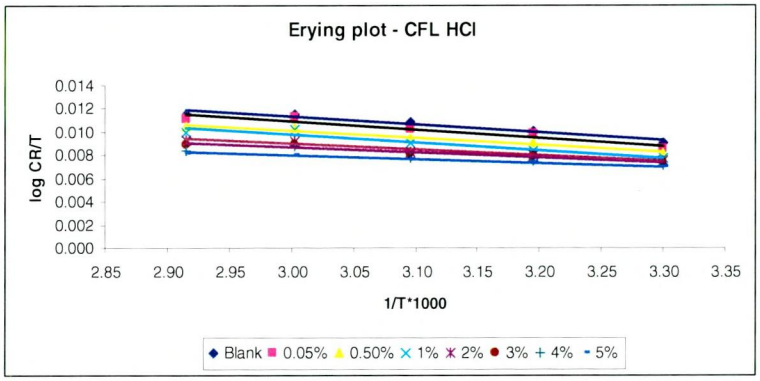


Figure 4.28

Erying plot for the mild steel dissolution in 1M HCl in the absence and in the presence of various concentrations of BSL extract at different temperatures

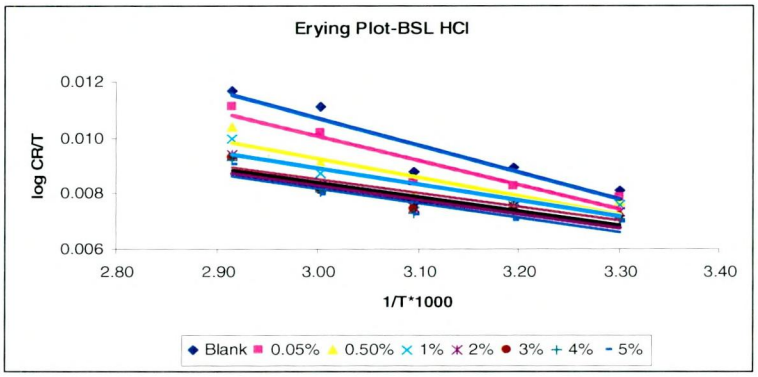
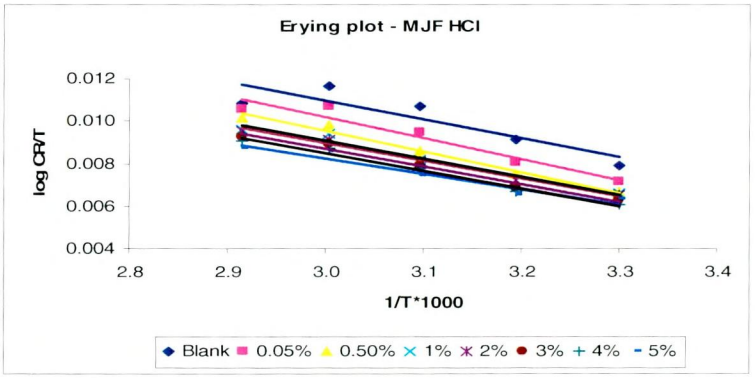


Figure 4.29

Erying plot for the mild steel dissolution in 1M HCl in the absence and in the presence of various concentrations of MJF extract at different temperatures



4.4.2 Arrhenius plot for HCl medium

The dependence of logarithm of the corrosion rate on the reciprocal of temperature (Arrhenius plot) is presented in the figures 4.30, 4.31 and 4.32 for CFL, BSL and MJF extracts respectively. Straight lines were obtained with correlation coefficient > 0.9. The activation energy E_a is calculated from the values of slope of these straight lines. The activation parameters for the dissolution of mild steel in 1M HCl in the presence of various concentrations of the CFL, BSL and MJF extract are given in tables 4.21, 4.22 and 4.23 respectively.

Figure 4.30

Arrhenius plot for the mild steel dissolution in 1M HCl in the absence and in the presence of various concentrations of CFL extract at different temperatures

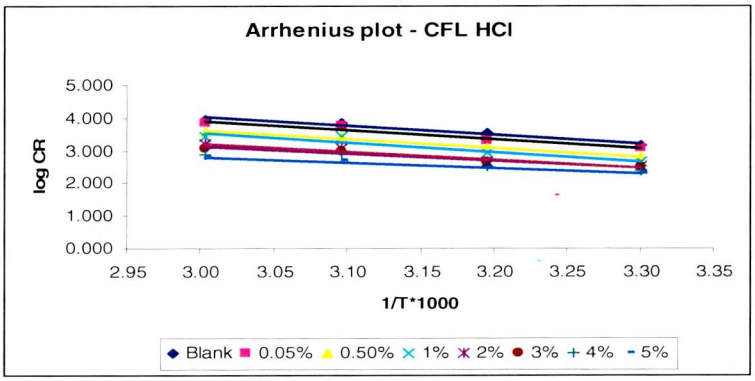


Figure 4.31

Arrhenius plot for the mild steel dissolution in 1M HCl in the absence and in the presence of various concentrations of BSL extract at different temperatures

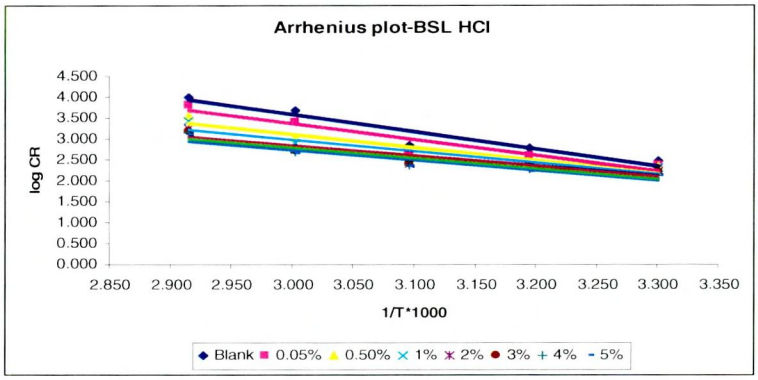
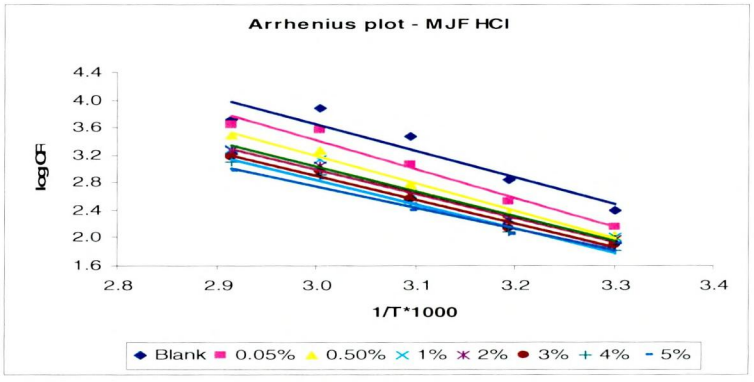


Figure 4.32

Arrhenius plot for the mild steel dissolution in 1M HCl in the absence and in the presence of various concentrations of MJF extract at different temperatures



Activation parameters

The activation energy E_a, Entropy of adsorption ΔS_{ads}, Enthalpy of adsorption ΔH_{ads} and heat of adsorption Q_{ads} in the case of pure 1M HCl and in presence of different concentrations of CFL, BSL and MJF are shown in tables 4.21, 4.22 and 4.23 respectively.

Table 4.21

Activation parameters for the dissolution of mild steel in 1M HCl in the absence and presence of various concentrations of CFL extract

Conc of the extract % v/v	-Ea kJ/mol	ΔS_{ads} J/K mol	$-\Delta H_{ads}$ kJ/mol	Q_{ads}
0.00	62.04	62.94	127.94	
0.05	62.58	62.94	132.26	0.57
0.5	56.82	63.00	118.10	-9.73
1.0	57.78	62.99	123.63	-6.46
2.0	48.13	63.08	97.12	-18.01
3.0	42.95	63.13	82.58	-23.72
4.0	39.49	63.16	74.02	-26.69
5.0	34.52	63.21	60.23	-31.51

Table 4.22

Activation parameters for the dissolution of mild steel in 1M HCl in the absence and presence of various concentrations of BSL extract

Conc of the extract % v/v	-Ea kJ/mol	ΔS_{ads} J/K mol	$-\Delta H_{ads}$ kJ/mol	Q_{ads}
0.00	79.06	62.79	183.83	
0.05	72.93	62.85	167.90	-23.17
0.5	59.84	62.98	130.41	-38.95
1.0	53.11	63.04	111.10	-45.36
2.0	47.18	63.10	95.12	-52.29
3.0	47.83	63.09	98.04	-43.51
4.0	47.22	63.10	96.80	-43.08
5.0	47.77	63. 09	99.37	-41.00

Table 4.23

Activation parameters for the dissolution of mild steel in 1M HCl in the absence and presence of various concentration of MJF extract

Conc of the extract % v/v	-Ea kJ/mol	ΔS_{ads} J/K mol	$-\Delta H_{ads}$ kJ/mol	Q_{ads}
0.00	73.76	62.83	169.63	
0.05	79.85	62.77	192.26	21.66
0.5	76.88	62.80	186.14	7.96
1.0	68.57	62.88	162.3	-7.07
2.0	67.36	62.90	159.14	-8.40
3.0	67.11	62.90	160.10	-8.36
4.0	67.17	62.90	161.55	-8.07
5.0	58.85	62.98	136.17	-12.23

The negative values of E_a indicate the adsorption of the extract molecules on the surface of mild steel. The increasing values of E_a suggest that the energy barrier for the corrosion reaction increases, suggesting that the inhibition efficiency increases in presence of the extracts. The increase in the activation energy in the presence of the extract when compared to that in the absence is suggestive of formation of adsorption film of physical nature. **(Popova *et al.*, 2003).**

The negative enthalpy change indicates that the adsorption process is exothermic in nature. From the tables, it is found that for all the extracts used, adsorption of the molecules on the mild steel surface in 1M HCl is exothermic.

The negative value of heat of adsorption also shows that the process of adsorption is exothermic at the higher concentrations. The heat of adsorption values < 80 kJ/mol suggests physical adsorption mechanism and > 80 kJ/mol suggests chemical adsorption **(Ita and Offiong, 2001).** The values < 80 kJ/mol confirms physical adsorption mechanism. The positive value of entropy may be attributed to the spontaneous adsorption of the phytochemical constituents of the extract on the surface of mild steel. The large and positive values of ΔS_{ads} suggest that the rate of adsorption of the components of the inhibitors on the mild steel surface is most likely to be controlled by the activation complex.

Thermodynamic functions

Thermodynamic functions for the dissolution of mild steel in 1M HCl in the absence and presence of various concentrations of the inhibitor were obtained by applying the Arrhenius equation and transition state equation.

Table 4.24

Thermodynamic functions for the dissolution of mild steel in 1M HCl in the absence and in the presence of various concentrations of CFL extract

Conc of the extract % v/v	$-\Delta G_{ads}$ kJ mol^{-1}				
	303 K	313 K	323 K	333 K	343 K
0.00	19.20	19.83	20.46	21.09	21.72
0.05	19.20	19.83	20.46	21.09	21.72
0.5	19.21	19.84	20.47	21.10	21.73
1	19.21	19.84	20.47	21.10	21.73
2	19.21	19.84	20.47	21.10	21.73
3	19.21	19.84	20.47	21.11	21.74
4	19.21	19.84	20.48	21.11	21.74
5	19.21	19.85	20.48	21.11	21.74

Table 4.25

Thermodynamic functions for the dissolution of mild steel in 1M HCl in the absence and in the presence of various concentrations of BSL extract

Conc of the extract % v/v	$-\Delta G_{ads}$ kJ mol^{-1}				
	303 K	313 K	323 K	333 K	343 K
0.00	19.21	19.83	20.46	21.09	21.72
0.05	19.21	19.83	20.46	21.09	21.72
0.5	19.21	19.84	20.47	21.10	21.73
1	19.21	19.84	20.47	21.10	21.73
2	19.21	19.84	20.47	21.10	21.73
3	19.21	19.84	20.47	21.10	21.73
4	19.21	19.84	20.47	21.10	21.73
5	19.21	19.84	20.47	21.10	21.73

Table 4.26

Thermodynamic functions for the dissolution of mild steel in 1M HCl in the absence and in the presence of various concentrations of MJF extract

Conc of the extract % v/v	$-\Delta G_{ads}$ kJ mol^{-1}				
	303 K	313 K	323 K	333 K	343 K
0.00	19.21	19.83	20.46	21.09	21.72
0.05	19.21	19.84	20.47	21.10	21.72
0.5	19.22	19.84	20.47	21.10	21.73
1	19.22	19.85	20.47	21.10	21.73
2	19.22	19.85	20.47	21.10	21.73
3	19.22	19.85	20.48	21.11	21.73
4	19.22	19.85	20.48	21.11	21.74
5	19.22	19.85	20.48	21.11	21.74

The negative value of ΔG_{ads} suggests that the adsorption of the inhibitor on the mild steel surface is spontaneous and the adsorbed layer is stable. According to **Quraishi *et al.*, (2000)** values of ΔG_{ads} upto -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and the charged surface (Physisorption). Those more negative than -40 kJ/mol or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (Chemisorption). The values of ΔG_{ads} (-19 to -22 kJ mol^{-1}) indicate that the extracts inhibit corrosion by physically adsorbing on the mild steel surface thus reducing the surface area available for corrosion.

4.5 Erying and Arrhenius plots for H_2SO_4 medium

4.5.1 Erying plot for H_2SO_4 medium

Erying plots for the mild steel dissolution in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of CFL, BSL and MJF extract at different temperatures are shown in figures 4.33, 4.34 and 4.35 respectively.

Figure 4.33

Erying plot for the mild steel dissolution in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of CFL extract at different temperatures

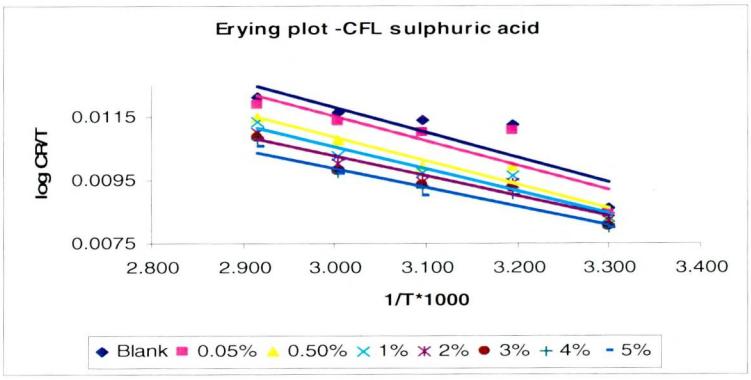


Figure 4.34

Erying plot for the mild steel dissolution in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of BSL extract at different temperatures

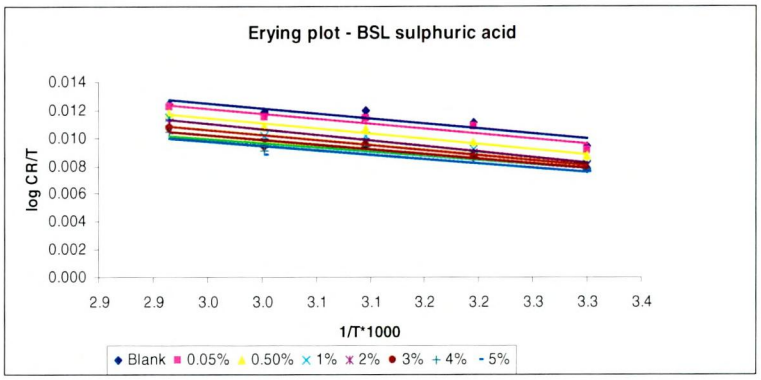
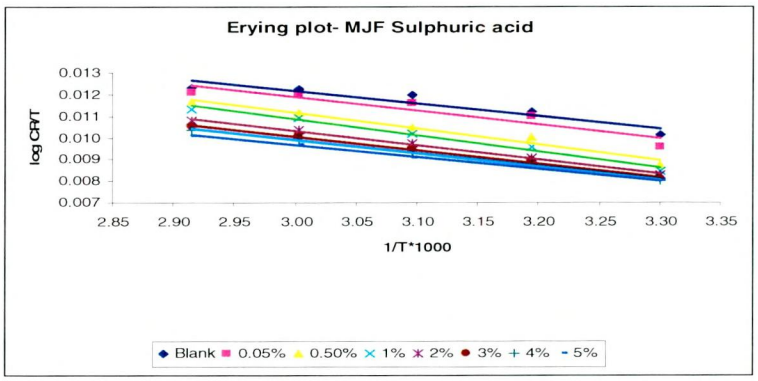


Figure 4.35

Erying plot for the mild steel dissolution in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of MJF extract at different temperatures



4.5.2 Arrhenius plots for H_2SO_4 medium

Arrhenius plots for the mild steel dissolution in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of CFL, BSL and MJF extracts at different temperatures are given respectively in figures 4.36, 4.37 and 4.38.

Figure 4.36

Arrhenius plot for the mild steel dissolution in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of CFL extract at different temperatures

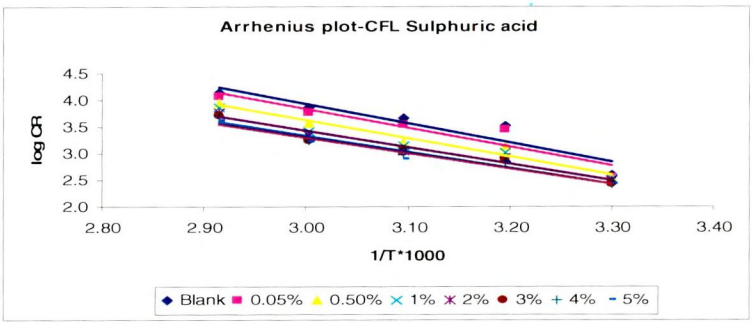


Figure 4.37

Arrhenius plot for the mild steel dissolution in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of BSL extract at different temperatures

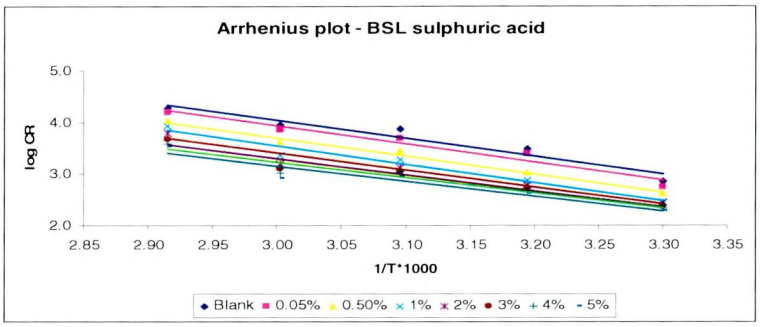
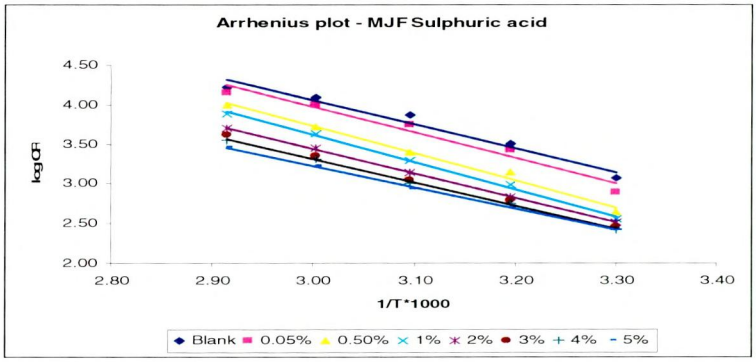


Figure 4.38

Arrhenius plot for the mild steel dissolution in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of MJF extract at different temperatures



The values of apparent corrosion activation energy (E_a), heat of adsorption (Q_{ads}), free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and the entropy change for the adsorption (ΔS_{ads}) are calculated for the studied system and are given in tables 4.27, 4.28 and 4.29 respectively.

Table 4.27

Activation parameters for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of CFL extract

Conc of the extract %v/v	-Ea kJ/mol	ΔS_{ads} J/K mol	$-\Delta H_{ads}$ kJ/mol	Q_{ads}
0.00	69.18	62.87	149.41	
0.05	67.99	62.88	147.04	-7.85
0.5	65.75	62.91	142.24	-16.58
1.0	61.99	62.95	131.53	-24.13
2.0	58.72	62.98	122.65	-27.73
3.0	58.75	62.98	123.87	-21.92
4.0	58.58	62.98	123.73	-22.01
5.0	55.45	63.01	114.68	-26.97

Table 4.28

Activation parameters for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of BSL extract

Conc of the extract %v/v	-Ea kJ/mol	ΔS_{ads} J/K mol	$-\Delta H_{ads}$ kJ/mol	Q_{ads}
0.00	66.47	62.90	137.91	
0.05	66.87	62.90	140.96	3.441
0.5	67.21	62.90	145.33	0.339
1.0	68.12	62.89	150.88	2.799
2.0	62.45	62.94	135.03	-5.883
3.0	59.65	62.97	128.22	-9.193
4.0	56.36	63.00	119.02	-13.111
5.0	55.57	63.01	117.67	-13.463

Table 4.29

Activation parameters for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of MJF extract

Conc of the extract %v/v	-Ea kJ/mol	ΔS_{ads} J/K mol	$-\Delta H_{ads}$ kJ/mol	Q_{ads}
0.00	57.84	62.98	109.51	
0.05	62.01	62.94	124.65	14.96
0.5	65.58	62.91	139.95	14.21
1.0	65.68	62.91	142.22	12.61
2.0	59.29	62.97	124.71	2.06
3.0	57.42	62.99	120.22	-0.47
4.0	56.22	63.0	117.49	-1.93
5.0	51.91	63.05	105.02	-5.85

The increase in energy of activation indicates the physical adsorption of CFL, BSL and MJF on the mild steel surface in 0.5M H_2SO_4.

The positive value of ΔS_{ads} shows that the reaction is spontaneous. The negative values of ΔH_{ads} indicate that the adsorption of extract molecules is an exothermic process. The negative values of Q_{ads} indicate that the adsorption of CFL in 0.5M H_2SO_4 on mild steel surface is exothermic. The heat of adsorption values are less than -40 kJ/mol in presence of CFL. Hence physical adsorption occurs **(Jha, 1990).** In presence of BSL and MJF, the values of Q_{ads} are positive at lower concentrations and when concentration increased the values became negative which indicate that the adsorption of the extract molecules of mild steel surface becomes endothermic at higher concentrations of these extract **(Umoren *et al.*, 2006).**

Table 4.30

Thermodynamic parameters for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of CFL extract

Conc of the extract %v/v	$-\Delta G_{ads}$ kJ mol^{-1}				
	303 K	313 K	323 K	333 K	343 K
0.00	19.20	19.83	20.46	21.09	21.71
0.05	19.20	19.83	20.46	21.09	21.72
0.50	19.20	19.83	20.46	21.09	21.72
1.00	19.20	19.83	20.46	21.09	21.72
2.00	19.21	19.84	20.47	21.10	21.72
3.00	19.21	19.84	20.47	21.10	21.73
4.00	19.21	19.84	20.47	21.10	21.73
5.00	19.21	19.84	20.47	21.10	21.73

Table 4.31

Thermodynamic parameters for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of BSL extract

Conc of the extract %v/v	$-\Delta G_{ads}$ kJ mol^{-1}				
	303 K	313 K	323 K	333 K	343 K
0.00	19.19	19.82	20.45	21.08	21.71
0.05	19.19	19.83	20.46	21.08	21.71
0.50	19.20	19.83	20.46	21.09	21.72
1.00	19.21	19.84	20.46	21.09	21.72
2.00	19.21	19.84	20.47	21.10	21.72
3.00	19.21	19.84	20.47	21.10	21.73
4.00	19.21	19.84	20.47	21.10	21.73
5.00	19.21	19.84	20.47	21.10	21.73

Table 4.32

Thermodynamic parameters for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of MJF extract

Conc of the extract %v/v	$-\Delta G_{ads}$ kJ mol^{-1}				
	303 K	313 K	323 K	333 K	343 K
0.00	19.19	19.82	20.45	21.08	21.71
0.05	19.20	19.83	20.46	21.08	21.71
0.50	19.20	19.83	20.46	21.09	21.72
1.00	19.20	19.83	20.46	21.09	21.72
2.00	19.21	19.84	20.47	21.10	21.72
3.00	19.21	19.84	20.47	21.10	21.73
4.00	19.21	19.84	20.47	21.10	21.73
5.00	19.21	19.84	20.47	21.10	21.73

The negative values of ΔG_{ads} indicate that adsorption of the extract on mild steel surface is spontaneous and the values ranging from 19 to 22 kJ/mol suggest physical adsorption mechanism.

Decrease in ΔG_{ads} (becomes more negative) with increasing temperature indicates the occurrence of endothermic process at which increasing temperature facilitates adsorption for all the three extracts in 0.5M H_2SO_4. Generally, an endothermic process is explicit to chemisorption and an exothermic process may be either physisorption or chemisorption (**Durnie *et al.*, 1999).**

4.6 Electrochemical studies

Corrosion process in aqueous solutions is electrochemical in nature. Measurements of current- potential relationships under controlled conditions give information on corrosion rate, inhibitor performance, coating performance and passive layer characteristics.

4.6.1 Polarization study for mild steel in 1M HCl

The polarization characteristics of a sample are measured by plotting the current response as a function of the applied potential. Since the current response varies over several orders of magnitude, the plot of logarithm of current against potential on a semi-log paper known as potentiodynamic polarization curve is obtained. Potentials positive to E_{corr} give anodic currents and potentials negative to E_{corr} give cathodic currents. **(Sastri, 1998).**

Potentiodynamic anodic and cathodic polarization scans were carried out for mild steel in 1M HCl in the absence and presence of 0.05%, 1%, 3% and 5% v/v concentrations of CFL, BSL and MJF extracts.

The polarization parameters such as Corrosion potential (E_{corr}), Corrosion current density (I_{corr}) and Tafel slopes (b_a and b_c) obtained by the extrapolation of the tafel lines and the linear polarization resistance (R_p) for the dissolution of mild steel in 1M HCl in the absence and presence of the extracts CFL, BSL and MJF are given in tables 4.33, 4.34 and 4.35 respectively.

Table 4.33

Electrochemical kinetic parameters for the dissolution of mild steel in 1M HCl in the absence and in the presence of various concentrations of CFL extract

Conc of the extract (%v/v)	$-E_{corr}$ mV	b_a mV/decade	b_c mV/decade	I_{corr} mA/cm^2	R_p Ω /cm^2	IE %	
						I_{corr}	R_p
0.00	518	246.73	247.78	14.48	4.17		
0.05	500	166.41	187.35	3.66	11.90	74.72	64.96
1	495	149.23	164.97	2.42	15.76	83.29	73.54
3	491	142.49	166.07	1.79	19.37	87.64	78.47
5	485	132.09	150.98	1.28	26.65	91.16	84.35

Table 4.34

Electrochemical kinetic parameters for the dissolution of mild steel in 1M HCl in the absence and in the presence of various concentrations of BSL extract

Conc of the extract (%v/v)	$-E_{corr}$ mV	b_a mV/decade	b_c mV/decade	I_{corr} mA/cm^2	R_p Ω /cm^2	IE %	
						I_{corr}	R_p
0.00	518	246.73	247.78	14.48	4.17		
0.05	506	183.26	209.32	5.7	8.46	60.63	50.71
1	495	137.43	159.58	1.9	18.60	86.88	77.58
3	488	120.94	146.24	0.89	35.94	93.85	88.39
5	487	118.6	146.48	0.79	39.59	94.54	89.47

Table 4.35

Electrochemical kinetic parameters for the dissolution of mild steel in 1M HCl in the absence and in the presence of various concentrations of MJF extract

Conc of the extract (%v/v)	$-E_{corr}$ mV	b_a mV/decade	b_c mV/decade	I_{corr} mA/cm^2	R_p Ω/cm^2	IE %	
						I_{corr}	R_p
0.00	518	246.73	247.78	14.48	4.17		
0.05	506	185.87	209.66	5.08	9.44	64.92	55.82
1	493	140.46	160.26	1.71	21.50	88.19	80.59
3	483	129.50	157.98	1.33	25.53	90.81	83.66
5	486	126.59	154.31	1.13	29.46	92.20	85.84

Corrosion is an electrochemical process and inhibitors decrease the velocity of electrochemical reactions.

From the electrochemical kinetic parameters given in table 4.33, 4.34 and 4.35 it is noted that, as the concentration of the extract increases, there is a marginal shift in E_{corr} and a decrease in I_{corr}. A low I_{corr} value in the presence of the extracts implies that the rate of electrochemical reaction were reduced due to the formation of a barrier layer over the surface of mild steel by the components of the extract. The adsorbed

inhibitor may not cover the entire metal surface, but occupies sites which are electrochemically active and thereby reduces the extent of anodic or cathodic reaction or both. The corrosion rate will be decreased in proportion to the extent to which the electrochemically active sites are blocked by the adsorbed inhibitor **(Sastri, 1998).**

It is noted from tables 4.33 and 4.34 that the values of i_{corr} decrease with increase in the concentration for the CFL and BSL extracts in 1M HCl. The decrease in i_{corr} with the extract concentration is associated with a shift in corrosion potential E_{corr} to less negative values. The addition of the extract hinders acid attack on the mild steel. This suggests that all the three extracts act as mixed type inhibitors. The highest efficiency of 94.54% is obtained with BSL.

From the R_p values given in tables 4.33, 4.34 and 4.35, it is seen that R_p increases with the increase in concentration of the extract, indicating the formation of an insulated adsorption layer. The extracts are effective at 5% v/v concentration providing an efficiency of 84 -89%. They inhibit corrosion by blocking the active sites of mild steel.

The polarization curves for the dissolution of mild steel in 1M HCl in the absence and in presence of CFL, BSL and MJF extracts are shown in figures 4.39, 4.40 and 4.41 respectively.

Figure 4.39

Potentiodynamic polarization curves for mild steel in 1M HCl for various concentrations of CFL extract

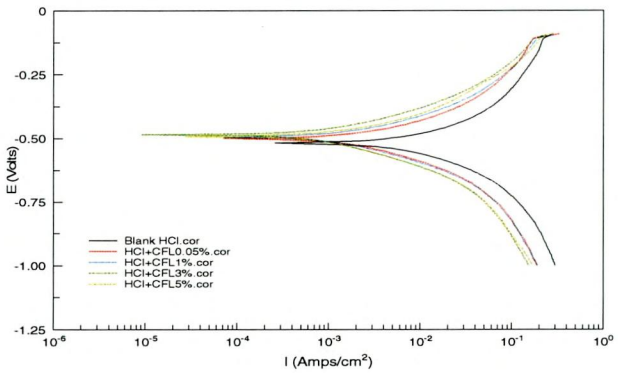


Figure 4.40

Potentiodynamic polarization curves for mild steel in 1M HCl for various concentrations of BSL extract

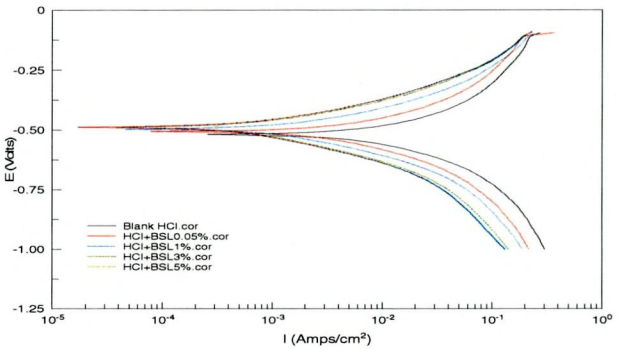
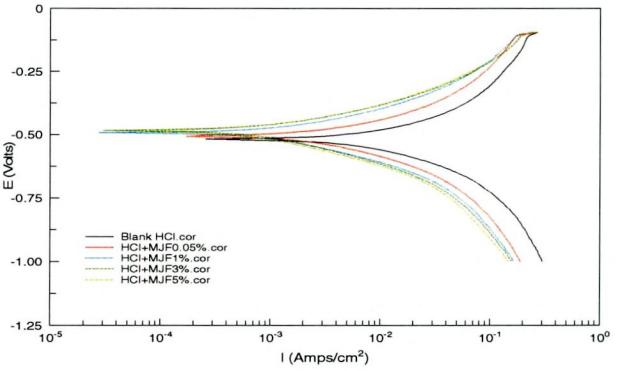


Figure 4.41

Potentiodynamic polarization curves for mild steel in 1M HCl for various concentrations of MJF extract



From the figures 4.39, 4.40 and 4.41 it is seen that the addition of the extract to the acid medium shifts the anodic polarization to more positive and the cathodic polarization to more negative values. The increase in concentration increases the polarization shifts. From the curves it is noted that the increase in concentration of the extracts gives rise to a consistent decrease in anodic and cathodic current densities for all the three extracts.

4.6.2 Electrochemical Impedance Spectroscopy studies

Electrochemical Impedance Spectroscopy becomes a very important tool in the study of inhibition of corrosion of metals. This method permits to superimpose a small sinusoidal excitation to an applied potential and then electrochemical interface metal/solution offers impedance. (**Violet Dayabaran *et al.*, 2005**).

Corrosion of metals in solutions is caused by charge transfer and mass transport at the metal/electrolyte interface. The electrochemical impedance method provides exact and rapid information about the kinetics of the electrode processes and the properties of the metal surface. Capacitance measurements provide information on adsorption and desorption processes, film formation on the electrode and the integrity of organic coatings **(Mansfeld *et al.*, 1982).**

4.6.2a Electro chemical study for Mild steel in 1M HCl

The impedance parameters namely the charge transfer resistance R_{ct} and double layer capacitance C_{dl} for the corrosion of mild steel in 1M HCl for different concentrations of CFL, BSL and MJF extracts evaluated using the Nyquist and Bode plots are given respectively in tables 4.36, 4.37 and 4.38.

Table 4.36

Impedance parameters for the corrosion of mild steel in 1M HCl for different concentrations of CFL extract

Conc of the extract (%v/v)	R_{ct} Ω	% IE	C_{dl} $\mu F/cm^2$	% IE
0.00	27.34		642	
0.05	60.88	55.09	232	63.86
1	83.61	67.30	202	68.53
3	124.6	78.06	165	74.29
5	204.89	86.65	137	78.66

The inhibition efficiency was calculated from R_{ct} and C_{dl} values of the impedance. The more densely packed the inhibitor surface film, the larger the diameter of the semicircle, which results in higher R_{ct} and lower C_{dl} values **(Mohammed A. Amin, 2006).**

An increase in the charge transfer resistance by 177Ω and a decrease in the double layer capacitance by 505 $\mu F/cm^2$ in the presence of CFL when compared to the blank solution indicate that there is formation of a highly nonporous protective film in the presence of the extract and hence a good inhibitive effect is noted.

Table 4.37

Impedance parameters for the corrosion of mild steel in 1M HCl for different concentrations of BSL extract

Conc of the extract (%v/v)	R_{ct} Ω	% IE	C_{dl} $\mu F/cm^2$	% IE
0.00	27.34		642	
0.05	38.84	29.61	284	56
1	111	75.37	200	69
3	210.85	87.03	156	76
5	233.17	88.27	131	80

Charge transfer resistance values given in table 4.37 show that for 5%v/v concentration of the extract, an increase of 206 Ω is obtained. The C_{dl} values decreased by 511 $\mu F/cm^2$ with 5% concentration of the extract which is indicative of

the formation of a thick double layer in the presence of the inhibitor thus reducing the dissolution of mild steel in the acidic medium.

Table 4.38

Impedance parameters for the corrosion of mild steel in 1M HCl for different concentrations of MJF extract

Conc of the extract (%v/v)	R_{ct} Ω	% IE	C_{dl} μF/cm^2	% IE
0.00	27.34		642	
0.05	42.50	35.67	296	54
1	72.25	62.16	222	75
3	84.78	67.75	162	65
5	156.58	82.54	159	76

As in table 4.38, the increase in the value of R_{ct} of about 129Ω and a 483 μF/cm^2 decrease in the C_{dl} value for 5%v/v of the extract lead to the increase in inhibition efficiency for MJF. The increase in R_{ct} value is attributed to the formation of protective film on the metal solution interface. The maximum efficiency obtained in presence of the extract is 83% for 5%v/v concentration of MJF.

It is noted from the values presented in the tables 4.36, 4.37 and 4.38 that the presence of the extract enhances R_{ct} values and reduces C_{dl} values. The decrease in C_{dl} may be due to the adsorption of the components in the extract to form a film on the surface of mild steel (**Larabi, 2004**) and the corrosion process involved is an activation controlled reaction (**Jayaperumal, 2010**).

The decrease in C_{dl} value is attributed to the increase in thickness of the double layer. The decreasing C_{dl} values also suggest a decrease in local dielectric constant between the mild steel and electrolyte induced by the adsorption of the inhibitor at the metal solution interface. (**McCafferty, 1972**).

The results of impedance measurement given by the Nyquist plots for mild steel in the absence and in the presence of various concentrations of CFL, BSL and MJF extracts in 1M HCl is shown in figures 4.42, 4.43 and 4.44 respectively.

Figure 4.42

Nyquist plots for mild steel in 1M HCl in the absence and in the presence of various concentrations of CFL extract

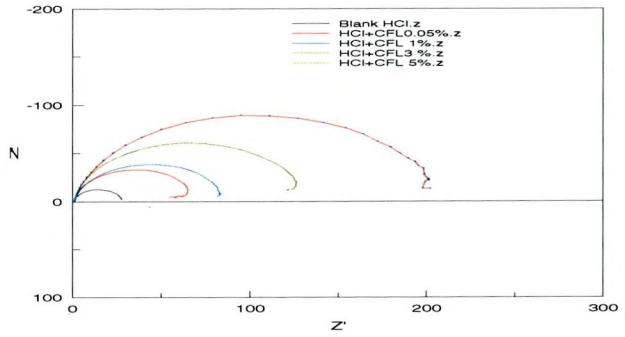


Figure 4.43

Nyquist plots for mild steel in 1M HCl in the absence and presence of various concentrations of BSL extract

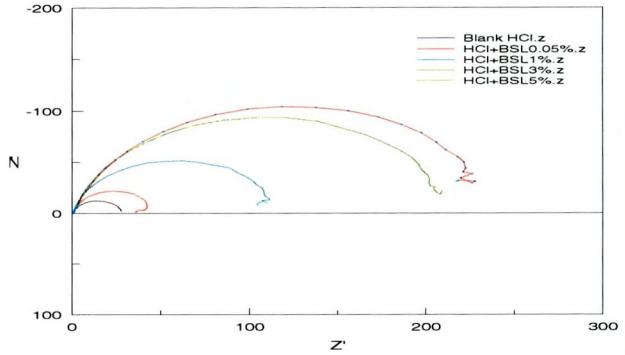
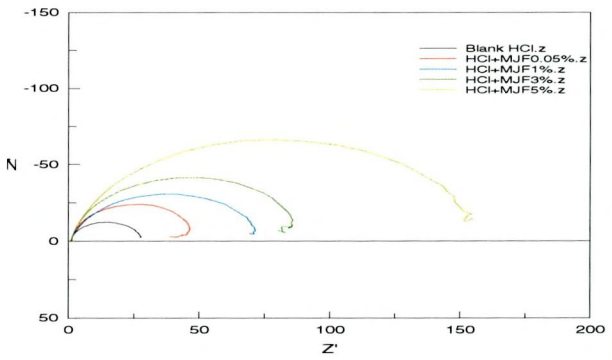


Figure 4.44

Nyquist plots for mild steel in 1M HCl in the absence and presence of various concentrations of MJF extract



The impedance diagrams are not perfect semicircles. This phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena (**Shih and Mansfeld, 1989).**

The diameter of the Nyquist plots increases on increasing the concentration of the extract as observed from the figures 4.42, 4.43 and 4.44. This suggested that the formed inhibitive film was strengthened by the addition of the extract. The Nyquist plots with no loops suggest that the mild steel – inhibitor system is under charge transfer resistance control and that the inhibitor is selectively adsorbed in specific places on the surface of mild steel (**Bastidas *et al*, 1997).**

Bode Plots

The frequency dependent behavior of an electrochemical system is more clearly described in the Bode plot. In this plot, the absolute impedance 1Z1 calculated from the equation $1Z1 = \sqrt{(Z')^2 + (Z'')^2}$ and the phase angle θ, of the resultant waveform are plotted as a function of the frequency.

Figure 4.45

Bode plots for mild steel in 1M HCl for various concentrations of CFL extract

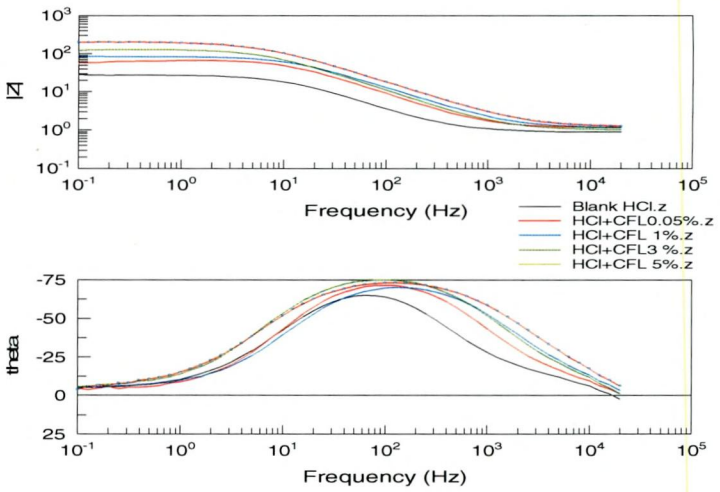


Figure 4.46

Bode plots for mild steel in 1M HCl for various concentrations of BSL extract

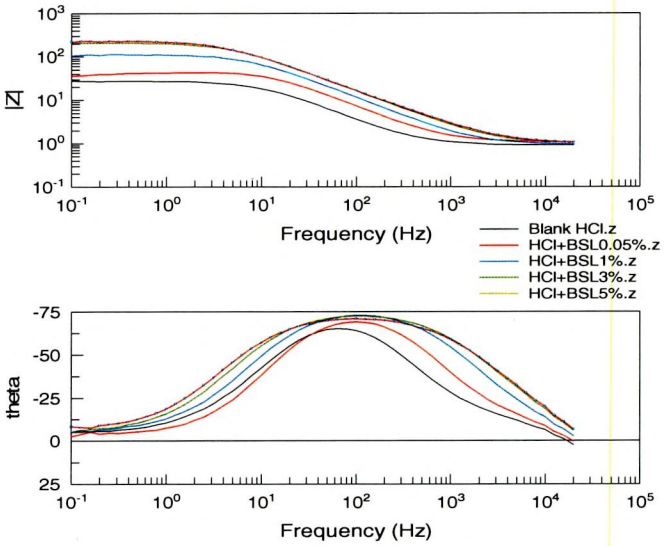
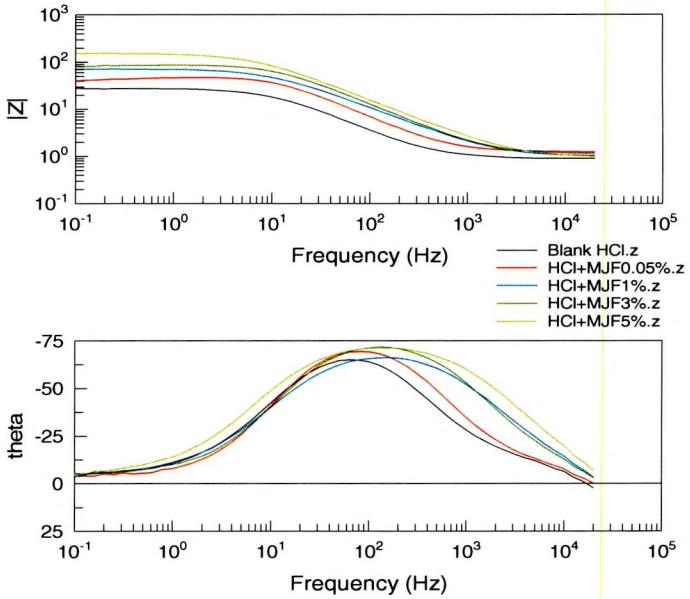


Figure 4.47

Bode plots for mild steel in 1M HCl for various concentrations of MJF extract



From the shape of the curves in figures 4.45, 4.46 and 4.47, it is interpreted that the adsorption of the extract molecules by the displacement of water takes place by a single step mechanism. Bode plots show only one time constant indicating the predominance of an activation phenomenon in the electrochemical process (**Touafri *et al.*, 2008).**

4.6.3 Polarisation study for mild steel in 0.5M H_2SO_4

The potentiodynamic polarization studies were carried out for mild steel in 0.5M H_2SO_4 in the absence and presence of different concentrations of the extracts.

The kinetic parameters namely Corrosion potential (E_{corr}), Corrosion current density (I_{corr}), Tafel slopes (b_a and b_c) obtained by the extrapolation of the tafel lines and polarization resistance (R_p) and the inhibition efficiencies for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and presence of the extracts CFL, BSL and MJF are given in tables 4.39, 4.40 and 4.41 respectively.

Table 4.39

Electrochemical kinetic parameters for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of CFL extract

Conc of the extract (%v/v)	$-E_{corr}$ mV	b_a mV/decade	b_c mV/decade	I_{corr} mA/cm^2	R_p Ω/cm^2	IE %	
0.00	525	270.1	312.44	11.27	6.02	I_{corr}	R_p
0.05	512	202.55	272.56	6.56	8.14	41.79	26.04
1	503	166.01	234.86	3.53	10.82	68.68	44.36
3	506	190.75	281.78	4.63	11.21	58.92	46.30
5	501	152.56	200.39	2.27	16.67	79.86	63.89

Table 4.40

Electrochemical kinetic parameters for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of BSL extract

Conc of the extract (%v/v)	$-E_{corr}$ mV	b_a mV/decade	b_c mV/decade	I_{corr} mA/cm^2	R_p Ω /cm^2	IE %	
						I_{corr}	R_p
0.00	525	270.1	312.44	11.27	6.02		
0.05	518	245.39	307.24	9.29	6.82	17.57	11.73
1	507	185.24	242.58	4.73	9.77	58.03	38.38
3	498	168.18	233.21	3.73	10.83	66.90	44.41
5	498	150.11	200.07	2.35	15.05	79.15	60.00

Table 4.41

Electrochemical kinetic parameters for the dissolution of mild steel in 0.5M H_2SO_4 in the absence and in the presence of various concentrations of MJF extract

Conc of the extract (%v/v)	$-E_{corr}$ mV	b_a mV/decade	b_c mV/decade	I_{corr} mA/cm^2	R_p Ω /cm^2	IE %	
						I_{corr}	R_p
0.00	525	270.1	312.44	11.27	6.02		
0.05	544	254.23	299	8.55	7.85	24.13	23.31
1	514	196.6	266.3	5.89	8.76	47.74	31.28
3	506	175.24	240.16	3.87	11.24	65.66	46.44
5	502	164.26	228.25	3.03	13.48	73.11	55.34

The values of b_a and b_c listed in tables 4.39, 4.40 and 4.41 in the absence and presence of various concentrations of CFL, BSL and MJF extract for the dissolution of mild steel in 0.5M H_2SO_4 decrease with increase in concentration of the inhibitor.

The change in values of b_a with increase in concentration of the extracts suggests that the components of the extract influence the anodic dissolution. The variation in the values of cathodic tafel slope b_c for all the three extracts for the dissolution of mild steel in 0.5M H_2SO_4 indicates that the components of the extract influence the kinetics of the hydrogen evolution reaction.

Damaskin (1971) has pointed out that the changes in slope in presence of the inhibitors may be attributed to

- Increased adsorption of organic substance
- A change in the mechanism of the process
- Formation of oxides on the metal surface in presence of oxidizing inhibitor and
- Gradual formation of compounds which are more effective inhibitors than the compounds initially adsorbed.

The values of i_{corr} decreases considerably with increase in concentration of the extract for all the three extracts in 0.5M H_2SO_4 as evident from the tables 4.39, 4.40 and 4.41. The decrease in i_{corr} with the extract concentration indicates a higher coverage of the extract molecules on the surface of mild steel with higher concentrations of the extract. As the concentration of extract increases, there is a marginal shift in E_{corr} and a decrease in I_{corr}. The addition of the extracts hinder the acid attack on the mild steel and a comparison of curves in both cases, shows that, with respect to the blank, increase in the extract concentration gives rise to decrease in anodic and cathodic current densities, suggesting mixed type of inhibition.(**Tamilselvi *et al.*, 2003).**

The R_p values increase with increase in concentration of the extract, indicating the formation of an insulated adsorption layer on mild steel immersed in 0.5 M H_2SO_4. This leads to an increase in efficiency with increase in concentration of the extract.

Potentiodynamic polarization curves for mild steel in 0.5M H_2SO_4 in the absence and presence of various concentrations of CFL, BSL and MJF extracts are shown respectively in figures 4.48, 4.49 and 4.50.

Figure 4.48

Potentiodynamic polarization curves for mild steel in 0.5M H_2SO_4 for various concentrations of CFL extract

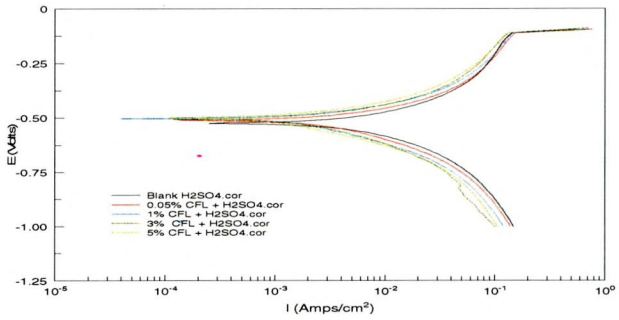


Figure 4.49

Potentiodynamic polarization curves for mild steel in 0.5M H_2SO_4 for various concentrations of BSL extract

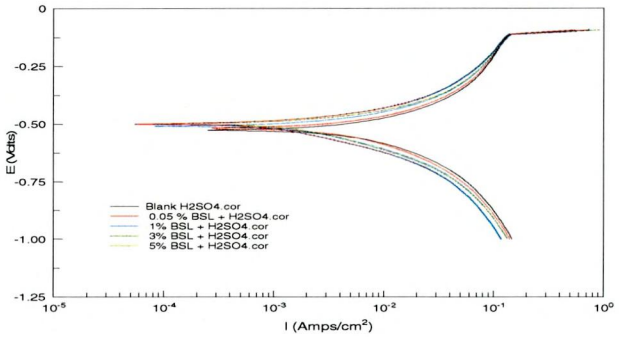
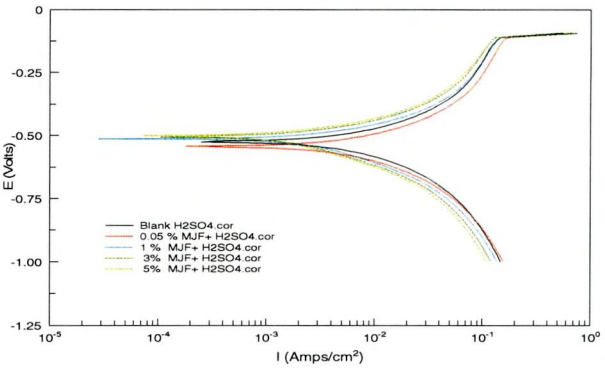


Figure 4.50

Potentiodynamic polarization curves for mild steel in 0.5M H_2SO_4 for various concentrations of MJF extract



The current densities in the presence of the extracts decreased as evident from the curves 4.48, 4.49 and 4.50.

4.6.4 Electrochemical study for mild steel in 0.5M H_2SO_4

Table 4.42

Impedance parameters for the corrosion of mild steel in 0.5M H_2SO_4 for different concentrations of CFL extract

Conc of the extract (%v/v)	R_{ct} Ω	% IE	C_{dl} μF/cm^2	% IE
0.00	8.61		316	
0.05	8.89	3.15	242	23.42
1	11.33	24.01	260	17.72
3	34.60	75.11	206	34.81
5	32.96	73.88	170	46.20

Table 4.43

Impedance parameters for the corrosion of mild steel in 0.5M H_2SO_4 for different concentrations of BSL extract

Conc of the extract (%v/v)	R_{ct} Ω	% IE	C_{dl} μF/cm^2	% IE
0.00	8.61		316	
0.05	14.61	34.14	287	9.18
1	22.19	49.98	237	25.00
3	27.27	46.40	233	26.26
5	29.22	80.92	190	39.87

Table 4.44

Impedance parameters for the corrosion of mild steel in 0.5M H_2SO_4 for different concentrations of MJF extract

Conc of the extract (%v/v)	R_{ct} Ω	% IE	C_{dl} $\mu F/cm^2$	% IE
0.00	8.61		415	
0.05	11.69	26.35	316	23.86
1	15.07	42.87	273	34.22
3	17.54	50.91	241	41.93
5	34.59	75.11	207	50.12

R_{ct} increases by 24 Ω and C_{dl} decreases by 146 $\mu F/cm^2$ providing 74% inhibition efficiency with the addition of 5% v/v concentration of CFL extract to the sulphuric acid medium. With 5%v/v concentration of BSL extract R_{ct} increases by 21 Ω and there is a decrease in C_{dl} by 126 $\mu F/cm^2$ which showed 81% protection against the dissolution of mild steel in sulphuric acid. The maximum R_{ct} value of 34.59Ω and minimum C_{dl} value of 207$\mu F/cm^2$ are obtained at 5% v/v concentration of MJF with a maximum inhibition efficiency of 75%.

The change in R_{ct} and C_{dl} values is due to the gradual replacement of water molecules by the anions of the acid and adsorption of the organic molecules on the mild steel surface reducing the extent of dissolution **(Muralidharan *et al.*, 1995).**

C_{dl} values tend to decrease with increase in concentration of the extract in all the three cases for the dissolution of mild steel in 0.5M H_2SO_4. Similar to the effect of the extracts on mild steel in HCl medium, the decrease in C_{dl} values can be attributed to the adsorption of extract molecules on the surface of mild steel.

Figure 4.51

Nyquist plots for mild steel in 0.5M H_2SO_4 for various concentrations of CFL extract

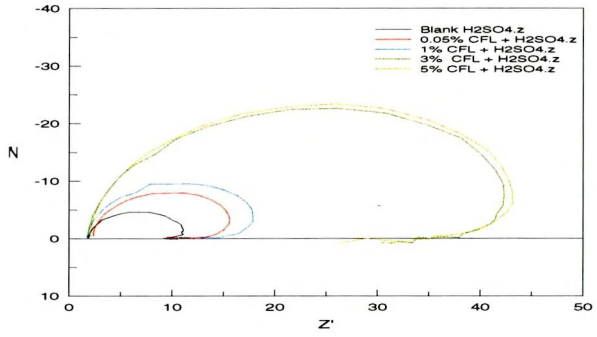


Figure 4.52

Nyquist plots for mild steel in 0.5M H_2SO_4 for various concentrations of BSL extract

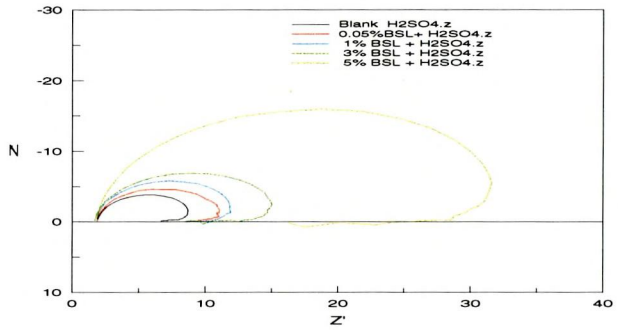
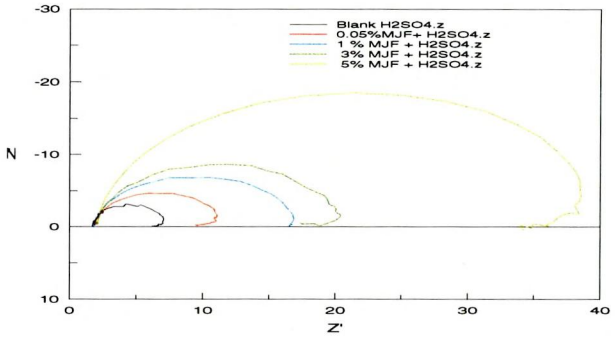


Figure 4.53

Nyquist plots for mild steel in 0.5M H_2SO_4 for various concentrations of MJF extract



It is noted from the Nyquist plots (figures 4.51, 4.52 and 4.53) that the charge transfer resistance value of mild steel in uninhibited sulphuric acid changes significantly after the addition of the extract. The more densely packed the inhibitor surface film, the larger the diameter of the semicircle, which results in higher R_{ct} and lower C_{dl} values. (**Mohammed A. Amin, 2006**).

A clean electrode without a passive film especially in the case of corroding electrode immersed in acid solutions give rise to an impedance spectrum consisting of perfect semicircle. The depressed semicircle is either due to the presence of pores on the electrode surface or due to the adsorption of the inhibitor. (**Szauer and Brandt, 1981**) In the present study, it is due to the adsorption of the extract molecules on the mild steel surface.

Figure 4.54

Bode plots for mild steel in 0.5M H_2SO_4 for various concentrations of CFL extract

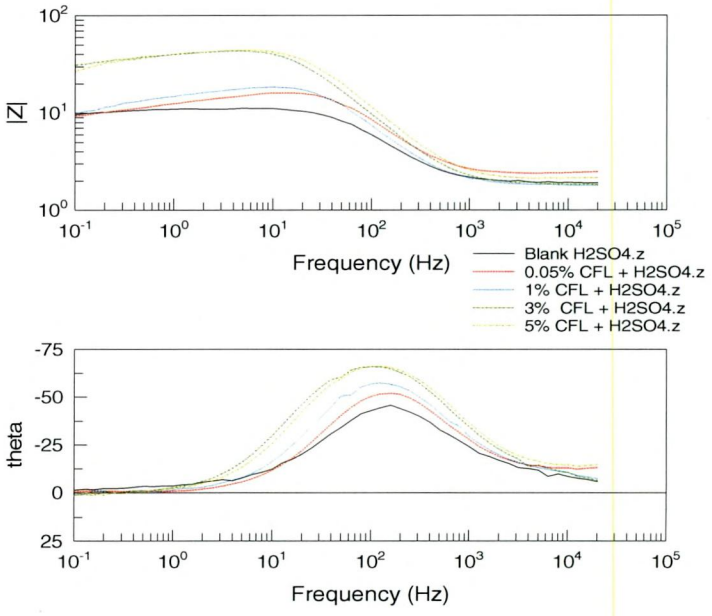


Figure 4.55

Bode plots for mild steel in 0.5M H_2SO_4 for various concentrations of BSL extract

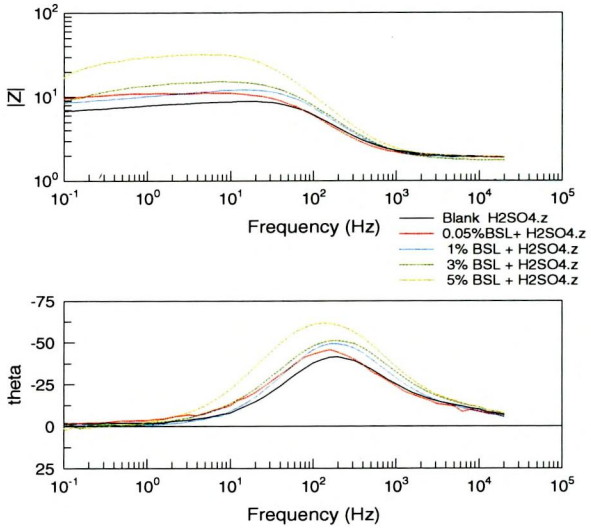
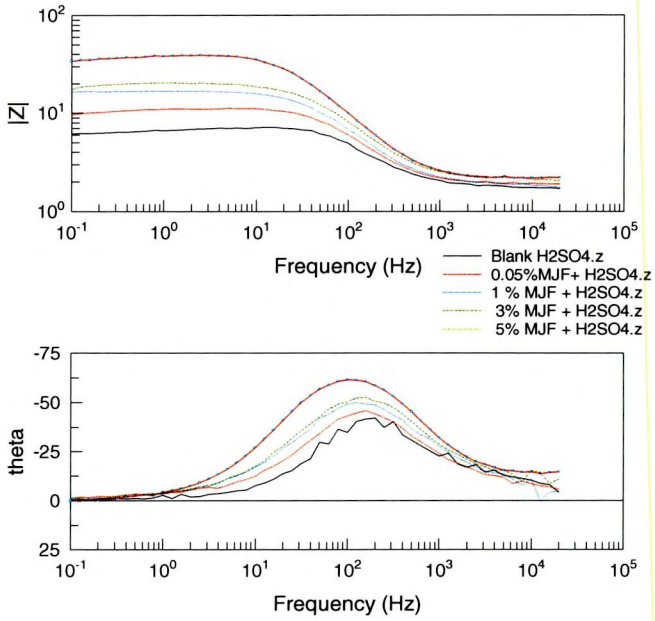


Figure 4.56

Bode plots for mild steel in 0.5M H_2SO_4 for various concentrations of MJF extract



Bode plots for all the three extracts show only one time constant indicating the predominance of an activation phenomenon in the electrochemical process as in HCl medium.

From the results obtained in the weight loss study and electrochemical studies, it is evident that the CFL, BSL and MJF extracts act as effective inhibitors for the dissolution of mild steel in 1M HCl and 0.5M H_2SO_4.

4.7 Comparison of results from Weight loss, Polarisation and Electro chemical impedance methods

The inhibition efficiencies of the extracts used for the dissolution of mild steel in 1M HCl and 0.5M H_2SO_4 by various methods namely weight loss; polarisation and electrochemical impedance methods are compared in table 4.45.

Table 4.45

Comparison of inhibition efficiencies obtained from Weight loss, Polarisation and Electro chemical impedance methods for the dissolution of mild steel in 1M HCl and 0.5M H_2SO_4 in presence of the extracts

Inhibitor	Conc %v/v	Percentage Inhibition efficiency									
		HCl					H_2SO_4				
		Weight loss method	Tafel extrapolation method	Linear polarization	Electrochemical impedance studies		Weight loss method	Tafel extrapolation method	Linear polarization	Electrochemical impedance studies	
					R_{ct}	C_{dl}				R_{ct}	C_{dl}
CFL	**0.05**	31.4	74.72	64.96	35.6	54	12.4	41.79	26.04	3.15	23
	1.0	59.9	83.29	73.54	62.1	65	17.7	68.68	44.36	24.0	18
	3.0	70.41	87.64	78.47	67.75	75	32.78	58.92	46.30	75.11	35
	5.0	77.56	91.16	84.35	82.54	75	34.41	79.86	63.89	73.88	46
BSL	**0.05**	18.43	60.63	50.71	29.37	56	20.85	17.57	11.73	34.14	9
	1.0	29.62	86.88	77.58	75.37	69	58.70	58.03	38.38	49.98	25
	3.0	48.45	93.85	88.39	87.03	76	67.52	66.90	44.41	46.40	26
	5.0	55.59	94.54	89.47	88.27	80	73.03	79.15	60.00	80.92	40
MJF	**0.05**	42.49	64.92	55.82	35.67	54	28.92	1.51	23.31	26.35	24
	1.0	59.66	88.19	80.59	62.16	75	69.00	47.74	31.28	42.87	34
	3.0	68.39	90.81	83.66	67.75	65	75.45	65.66	46.44	50.61	42
	5.0	75.21	92.20	85.84	82.54	76	78.91	73.11	55.34	75.11	50

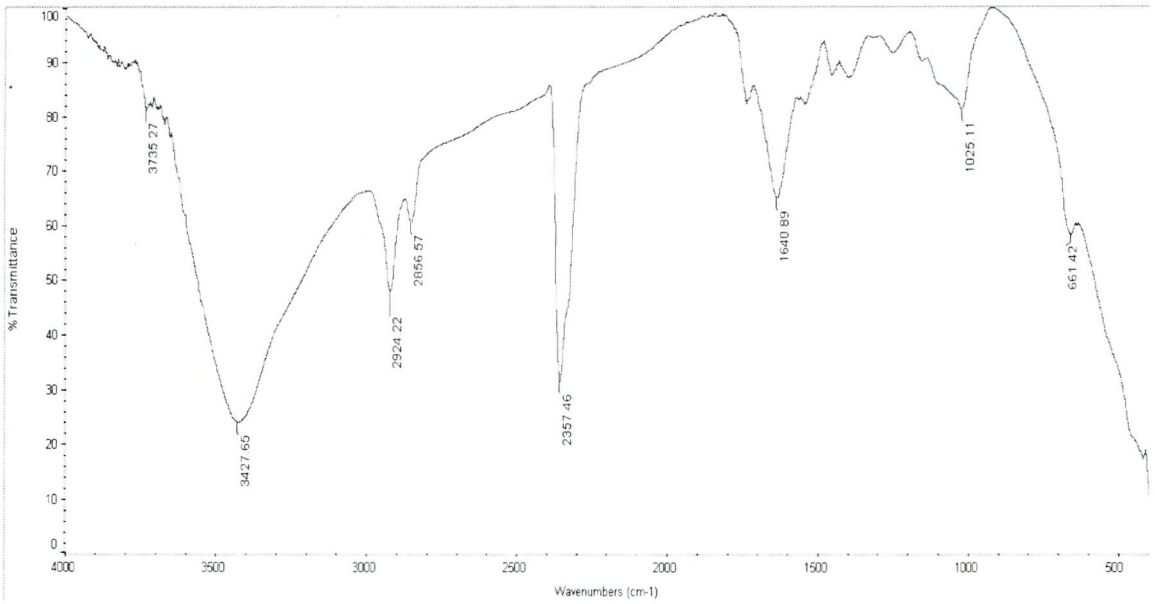
From table 4.45, it is evident that the IE obtained in all the methods increase with increase in concentration of the inhibitors in both 1M HCl and 0.5M H_2SO_4 media. The magnitude of the inhibition efficiencies obtained by different methods varies. The variation can be attributed to the fact that the weight loss method gives average corrosion rate, whereas electrochemical methods give instantaneous rates **(Libin Tang *et al.*, 2006).** These differences may also be expected to arise because of the difference in the time required to form an adsorbed inhibitor layer on the metal surface that is capable of corrosion inhibition. Eventhough the magnitude of the efficiency obtained by different methods varies, the trend of increase in inhibition efficiency with increase in concentration of the extracts was noted in all the methods.

4.8 FTIR studies

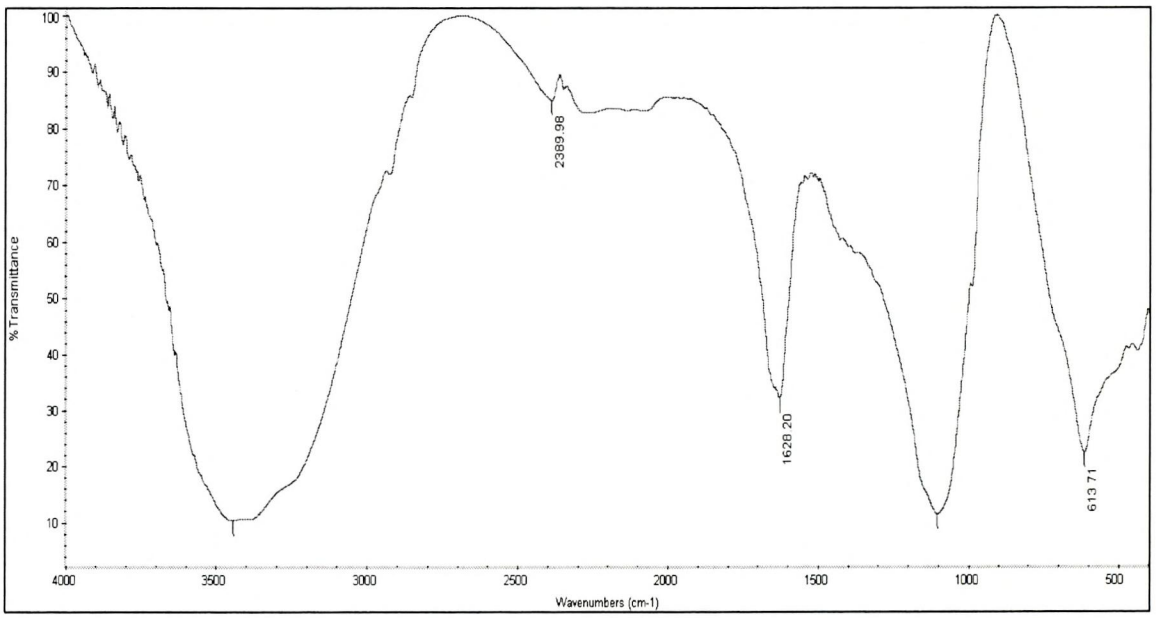
Several researchers have confirmed that FTIR spectra can be used to determine the type of bonding for the organic molecules adsorbed on the metal surface. The FTIR spectra obtained for the powdered inhibitor and the protective films formed on the surface of the mild steel with 5% v/v concentration of CFL, BSL and MJF in 1M HCl and 0.5M H_2SO_4 has been analyzed by FTIR spectroscopy and are given in the figures 4.57, 4.58 and 4.59 respectively.

Figure 4.57

a) FTIR spectra of CFL



b) FTIR spectra of the surface film formed by the corrosion of mild steel in 1M HCl in the presence of 5% v/v of CFL extract



c) FTIR spectra of the surface film formed by the corrosion of mild steel in 0.5M H_2SO_4 in the presence of 5% v/v of CFL extract

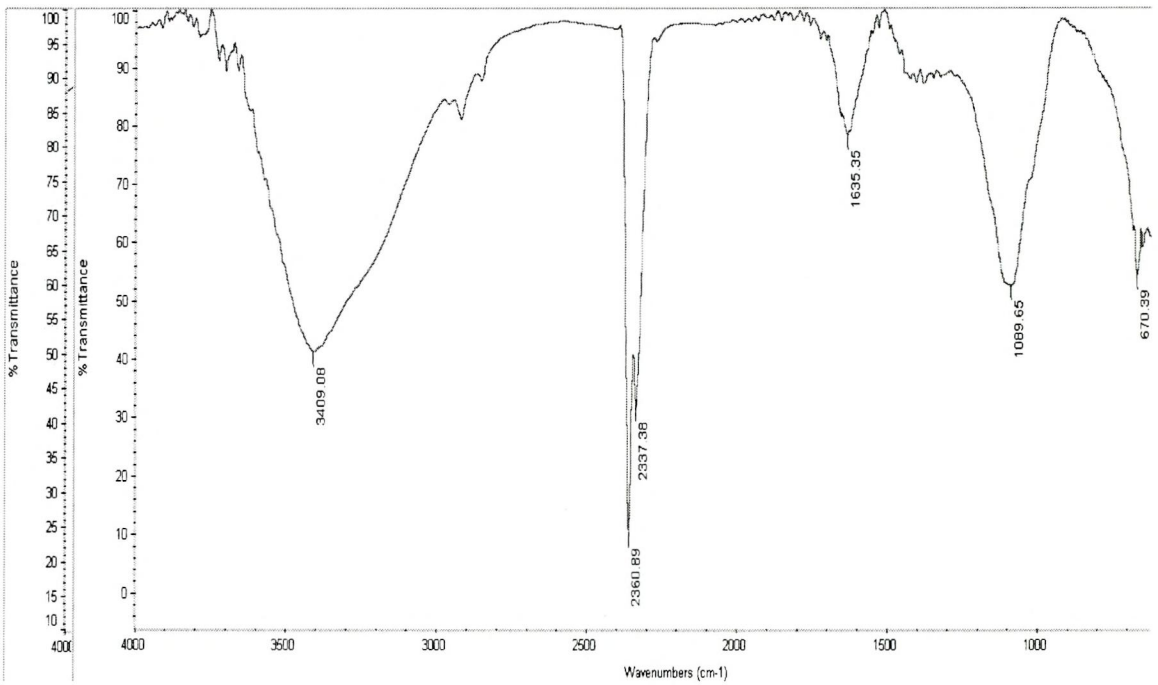
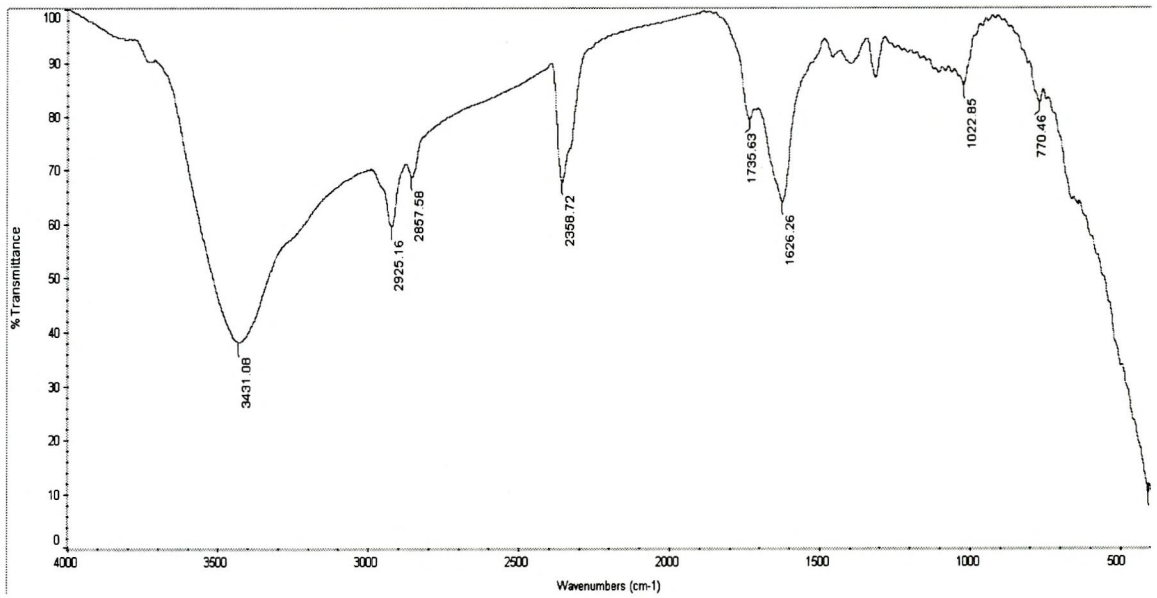
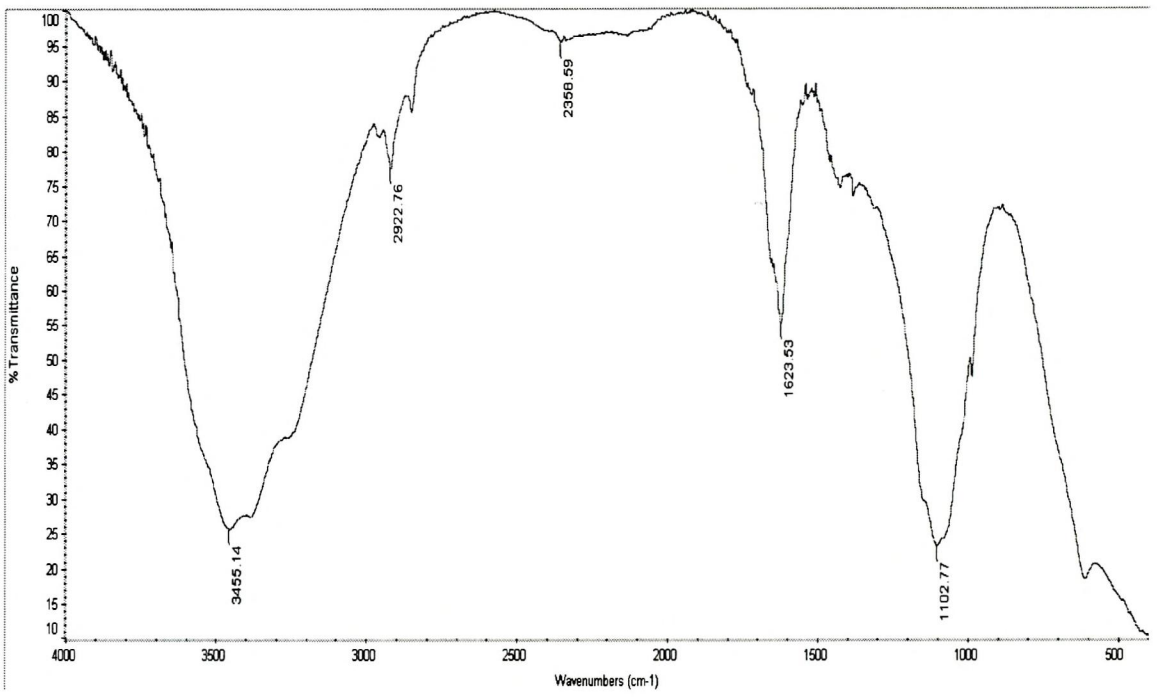


Figure 4.58

a) FTIR spectra of BSL



b) FTIR spectra of the surface film formed by the corrosion of mild steel in 1M HCl in the presence of 5% v/v of BSL extract



c) FTIR spectra of the surface film formed by the corrosion of mild steel in 0.5M H_2SO_4 in the presence of 5% v/v of BSL extract

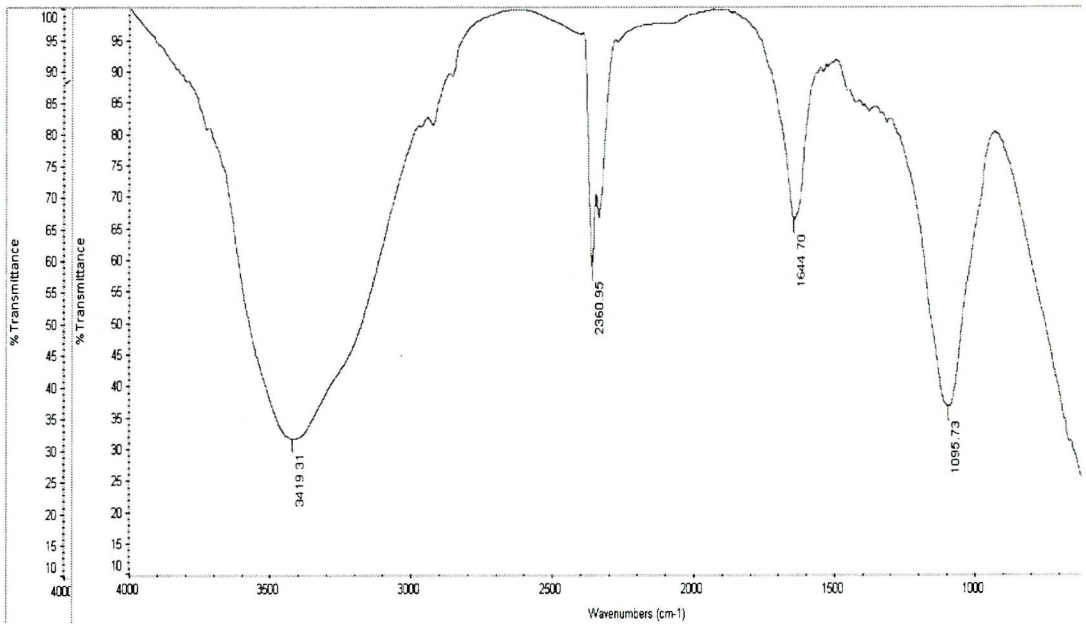


Figure 4.59

a) FTIR spectra of MJF

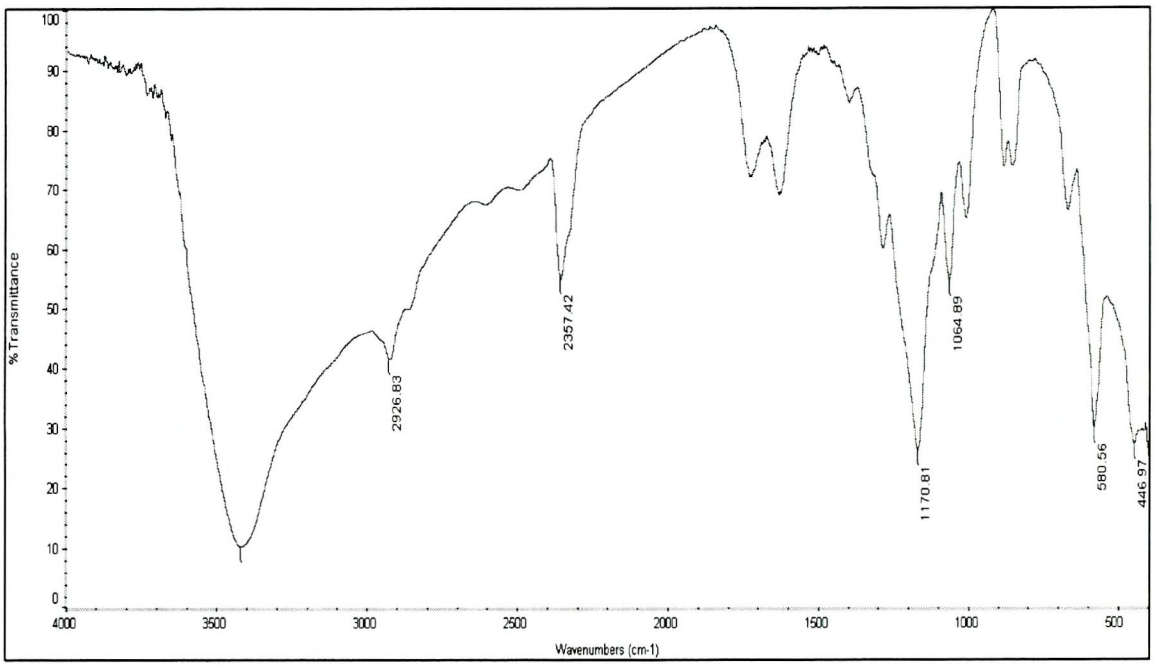


Table 4.47

IR bands for pure *Bougainvillea spectabilis* leaf powder and the adsorbed layer of BSL in 1M HCl and 0.5M H_2SO_4

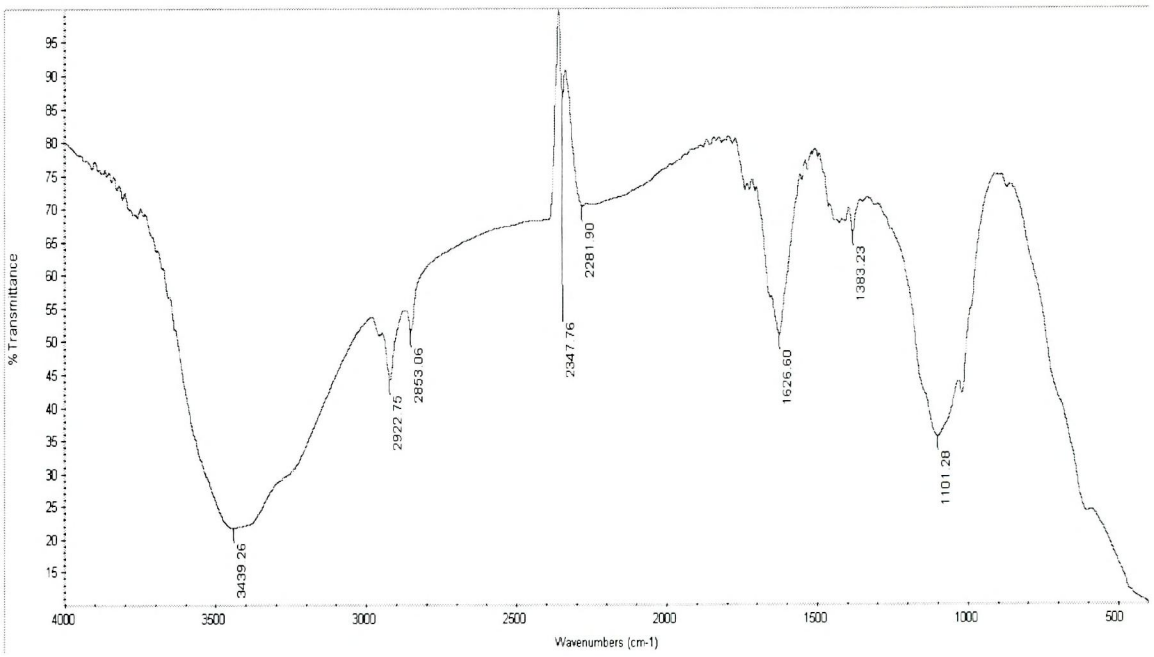
Frequency of asorption cm^{-1}			Assignment
BSL powder	**5% BSL in HCl**	**5% BSL in H_2SO_4**	
3431.08	3455.14	3419.31	O-H stretching
2925.16	2922.76		Aliphatic C-H stretching
2857.58			
2358.72		2360.95	$N\text{-}H^+$ stretching
1735.63			C=O stretching
1626.26	1623.53	1644.70	C=C stretching
1022.85	1102.77	1095.73	C-O-C asymmetric vibration

Table 4.48

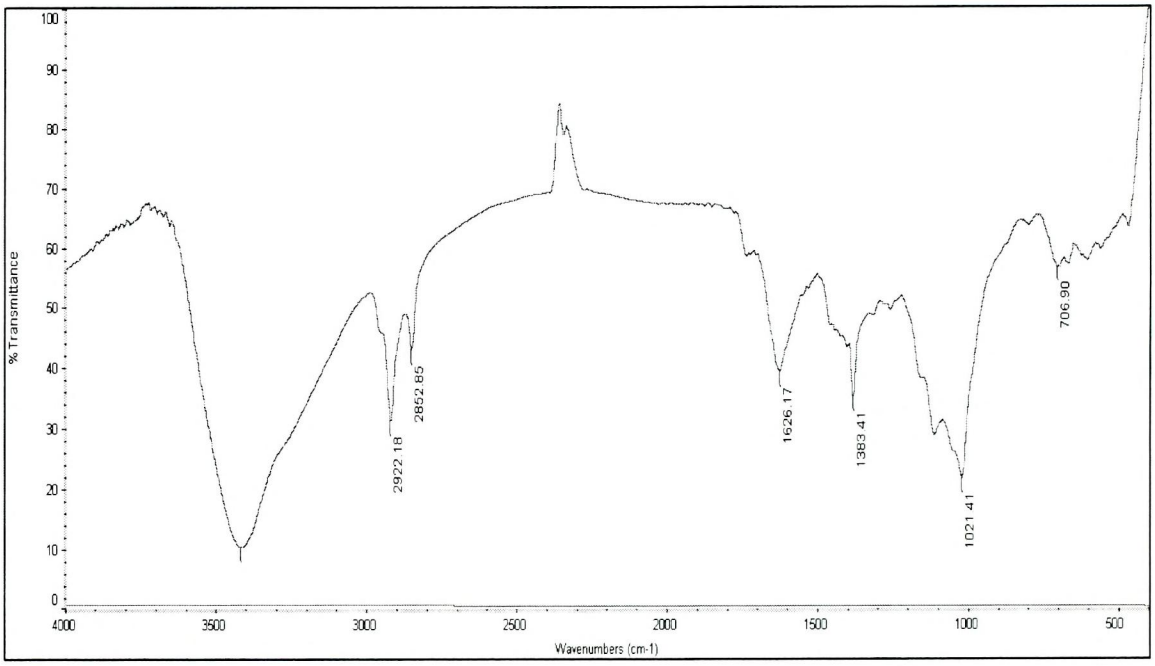
IR bands for pure *Mirabilis jalapa* flower powder and the adsorbed layer of MJF in 1M HCl and 0.5M H_2SO_4

Frequency of asorption cm^{-1}			Assignment
MJF powder	**5% MJF in HCl**	**5% MJF in H_2SO_4**	
3410	3439.26	3420.19	O-H stretching
2926.63	2922.75,w 2653.06,w	2922.18, 2852.85	Aliphatic C-H stretching
2357.42			$N\text{-}H^+$ stretching
1170.81			
1064.89	1101.28	1021.41	C-O-C asymmetric vibration
580.56			

b) FTIR spectra of the surface film formed by the corrosion of mild steel in 1M HCl in the presence of 5% v/v of MJF extract



c) FTIR spectra of the surface film formed by the corrosion of mild steel in 0.5M H_2SO_4 in the presence of 5% v/v of MJF extract



The assignments of IR peaks are given in table 4.46, 4.47 and 4.48 for CFL, BSL and MJF respectively.

Table 4.46

IR bands for pure *Cassia fistula* leaf powder and the adsorbed layer of CFL in 1M HCl and 0.5M H_2SO_4

Frequency of asorption cm^{-1}			Assignment
CFL powder	**5% CFL in HCl**	**5% CFL in H_2SO_4**	
3427.65	3430	3409.08	O-H stretching
2924.22			Aliphatic C-H stretching
2856.57			
2357.46		2360.69,2337.38	$N\text{-}H^+$ stretching
1640.89	1628.20	1635.35	C=C or C=N stretching
1025.11	1100	1069.65	C-O-C asymmetric vibration
661.42	613.71	670.39	aromatic C=C or C-H bending

As noted in table 4.48, the weak bands at 2924 cm^{-1} and 2856 cm^{-1} in the spectra of CFL are attributed to the aliphatic C-H stretching vibrations. From the figure 4.58 a, b and c, it is clear that the peak noted at 3427.65 cm^{-1} which is due to the O-H stretching has shifted to 3430 cm^{-1} and 3409.08 cm^{-1} in case of the adsorbed layers. The peak at 1640.89 cm^{-1} has shifted slightly which shows physical adsorption. The peak observed at 1025.11cm^{-1} is attributed to the C=C or C=N stretching. The shift in this peak to 1100 cm^{-1} and 1069.65 cm^{-1} show that a bond has formed between Fe and lone pair of oxygen present in the constituents.

Table 4.47 shows the peaks noted in the spectra of BSL and the assignment of the peaks to the corresponding vibrations. The peak at 2925.16 cm^{-1} is assigned to the alkane C-H stretching present in the inhibitor component. The peak at 3455.14 cm^{-1} is due to the O-H stretching. The peak at 1022.85 cm^{-1} has shifted to 1102.77 cm^{-1} and 1095.73 cm^{-1} in HCl and H_2SO_4 respectively. The large shift in the peak shows that there is chemisorption of the constituents through the bonds formed by lone pair of electrons on the oxygen with Fe in the mild steel.

The spectra of MJF (figures 4.60 a, b and c) show similar peaks with a slight shift in their positions. A peak at 3410 cm^{-1} due to the O-H stretching shows a shift to 3439 and 3420 cm^{-1} (table 4.48) in the adsorbed layers. The shift in peaks and the appearance of similar peaks in the extract and the adsorbed layers indicate that there is interaction between the extract and Fe in mild steel.

The FTIR spectra showed variation in presence of all the three extracts (5%v/v). Most of the peaks observed in the spectra of powdered extract were also noted in the surface film suggesting that adsorption of the phytochemical constituents on the mild steel surface takes place. The greater shifts in case of few peaks confirm that the adsorption is physical leading to chemisorption. The shift in the peaks due to O-H stretching in all the spectra confirms the formation of Fe –extract constituent complex.

4.9 Mechanism of inhibition

Iron corrodes in HCl forming ferrous chloride and hydrogen according to the equation

$$Fe + 2HCl \longrightarrow FeCl_{2(aq)} + H_{2(g)}$$

The reaction can be written as

$$Fe_{(metal)} + water \longrightarrow Fe^{2+}_{(aq)} + 2e^- \text{ (metal)}$$

$$2HCl \longrightarrow 2Cl^- + 2H^+$$

$$2e^- \text{ (metal)} + 2H^+ \longrightarrow H_{2(g)}$$

In hydrochloric acid solution the following mechanism is proposed for the corrosion of iron and steel (**Morad *et al.*, 1995**)

$$Fe + Cl^- \longrightarrow FeCl^-_{ads}$$

$$FeCl^-_{ads} \longrightarrow FeCl_{ads} + e^-$$

$$FeCl_{ads} \longrightarrow FeCl^+ + e^-$$

$$FeCl^+ \longrightarrow Fe^{2+} + Cl^-$$

$$Fe + H^+ \longrightarrow FeH^+_{ads}$$

$$FeH^+_{ads} + e^- \longrightarrow FeH_{ads}$$

$$FeH_{ads} + H^+ + e^- \longrightarrow Fe + H_2$$

According to the mechanism for the anodic dissolution of Fe in acidic sulphate solutions proposed by **Bockris *et al*, (1961)** Fe electro-dissolution in acidic sulphate solutions depend primarily on the adsorbed intermediate $FeOH_{ads}$

$$Fe + OH^- \longrightarrow FeOH_{ads} + H^+ + e^-$$

$$FeOH_{ads} \longrightarrow FeOH^+ + e^-$$

$$FeOH^+ + H^+ \longrightarrow Fe^{2+} + H_2O$$

Cathodic hydrogen evolution follows the steps

$$Fe + H^+ \longrightarrow (FeH^+)_{ads}$$

$$(FeH^+)_{ads} + e^- \longleftrightarrow (FeH)_{ads}$$

$$(FeH)_{ads} + H^+ + e^- \longrightarrow Fe + H_2$$

The corrosion rate of Fe in H_2SO_4 solutions is controlled by both hydrogen evolution reaction and dissolution reaction of Fe.

Corrosion inhibitors reduce or prevent these reactions by adsorbing on the surface of the metal and act by forming a barrier by complexing with metal ions. Some of the inhibitors facilitate the formation of a passive film on the metal surface **(Quraishi *et al.*, 2005).**

The inhibitive effect of some plant extracts is due to the adsorption of the phytochemical constituents present in the extract on the surface of the metal, which protect the metal surface and thus do not permit the corrosion process to take place **(Zakvi and Mehta, 1988).** The adsorption depends on the chemical structure of the components in the inhibitor, the charge on the metal surface and the nature of the medium.

Adsorption of the inhibitor molecules may be explained by the presence of an oxygen atom, electron of aromatic rings and electron donating groups. The planarity of π and lone pair of electrons present on heteroatoms are the important structural features that determine the adsorption of these molecules on the metal surface. The atom at which a higher electron density exists will become the point of adsorption and there can be more than one point of adsorption also depending upon the stereochemistry of the inhibitor molecule. Many workers have explained the efficiency of the inhibitors on the basis of this molecular structure.

Mechanism involving two adsorbed intermediate has been discussed for the retardation of Fe anodic dissolution in presence of an inhibitor molecule(Y).

$$Fe + H_2O \longrightarrow Fe.\,H_2O_{(ads)}$$

$$Fe.H_2O_{(ads)} + Y \longrightarrow FeOH^-_{(ads)} + H^+ + Y$$

$$Fe.H_2O_{(ads)} + Y \longrightarrow FeY_{ads} + H_2O$$

$$FeOH^-_{ads} \longrightarrow FeOH_{(ads)} + e^-$$

$$FeY_{ads} \longrightarrow FeY^+_{ads} + e^-$$

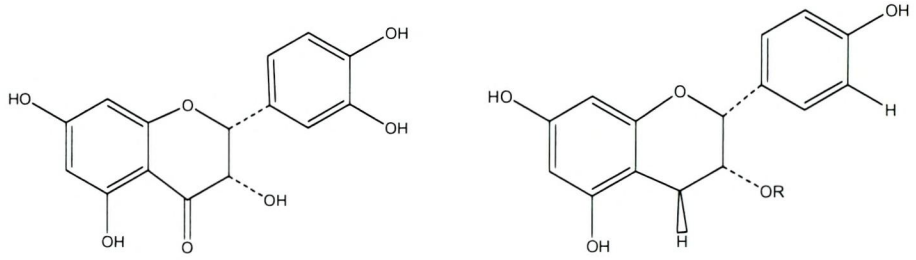
$$FeOH^+ + H^+ \longrightarrow Fe^{2+} + H_2O$$

It is known that mild steel has coordination affinity to sulphur, nitrogen and oxygen containing ligands. Generally, the adsorption of organic molecules involves the O, N and S atoms. Heteroatoms such as nitrogen, oxygen and sulphur are capable of forming coordinate covalent bond with metal owing to their free electron pairs and thus, acting as inhibitor **(Flick, 1993).** This process may block the active sites and hence decrease the corrosion rate. The inhibitor molecules contain these atoms and could be adsorbed on the metal surface and decrease the surface area available for a cathodic and/ or anodic reaction to take place. In acidic solution, the active constituent present in the inhibitor exist as protonated species adsorb on the cathodic sites of mild steel and decreases the evolution of hydrogen. The adsorption on anodic sites occurs through π electrons and lone pair of electrons on nitrogen atom of the active component found in the inhibitor.

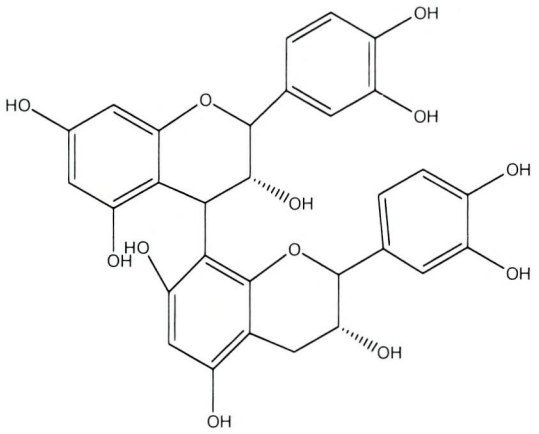
The CFL extract was spot tested for alkaloids, terpenoids, flavonoids, tannins, phenols, steroids, saponins and carbohydrates. The tests confirmed the presence of alkaloids, flavonoids and carbonyl group. **Bahorun *et al.*, 2005** has reported the presence of (-) epiafzelechin, (-) epiafzelechin-3-O glucoside, (-) epicatechin, procyanidin B2, biflavonoids, triflavonoids, rhein, rhein glucoside, sennoside A, sennoside B, chrysophanol, physcion, etc. The structures of these components are given in figure 4.60. **(Kashiwada *et al.*, 1996; Kaji *et al.*, 1968; Mahesh *et al.*, 1984)**.These constituents mostly comprise of oxygen and hydroxyl groups. The adsorption of these components takes place through these active centres. They may also form complexes with the metal cation. These complexes formed block the metal surface thus reducing the inhibition efficiency.

Figure 4.60

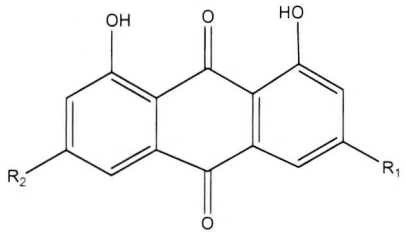
Structure of phytoconstituents of *Cassia fistula*



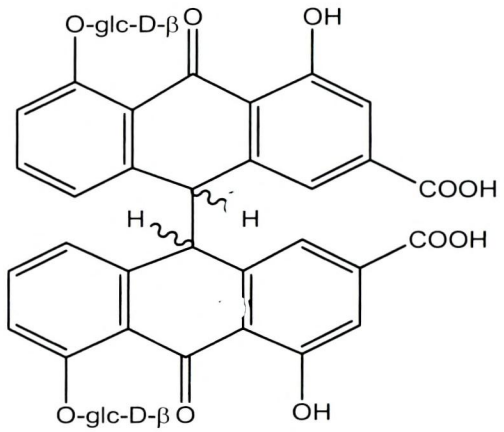
a. (-)Epicatechin **b. Epiafzelechin**



c. Procyanidin B2



d. Rhein

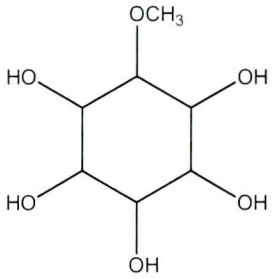


e. Sennoside A and B

The BSL extract was spot tested for alkaloids, terpenoids, flavonoids, tannins, phenols, steroids, saponins and carbohydrates. The tests confirmed the presence of alkaloids, flavonoids and tannins. The constituents reported in the leaves of Bougainvillea spectabilis are D- pinitol (3-*O*-methylchiroinositol), tannins, flavonoids and alkaloids (**Meenakshi Bhat *et al.*, 2009**). The structures of the constituents of BSL are given in figure 4.61. The inhibition of mild steel dissolution in the acidic medium is due to the formation of complexes with Fe through the electronegative atoms present in these constituents that block the anodic and cathodic points on the surface of mild steel. It has been shown that the inhibitory action of some plant extracts is due to the presence of tannin in their chemical constitution (**Martinez and Stern, 2002).** Even in very acidic solution, the inhibitive action of tannin was attributed to the formation of a passivating layer of ferric-tannates on the metal surface **(Saleh *et al.*, 1982)**

Figure 4.61

Structure of phytoconstituents of *Bougainvillea spectabilis*

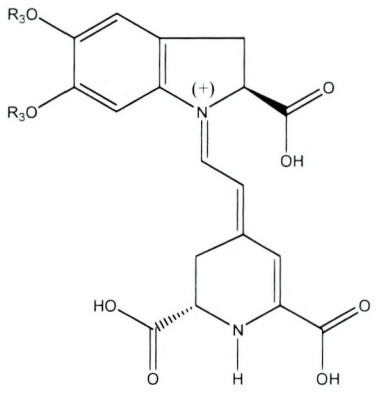


D-Pinitol

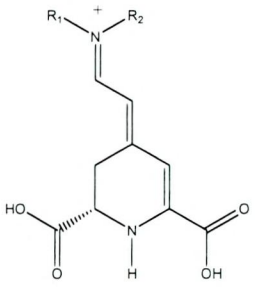
The MJF extract was spot tested for alkaloids, terpenoids, flavonoids, tannins, phenols, steroids, saponins and carbohydrates. The presence of alkaloids and flavonoids was confirmed by the test. Literature cites the presence of betaxanthin, betacyanin and betalains (figure 4.62) which are responsible for the colour of its flowers (**Salisbury *et al.*, 1991).** These constituents contain >NH and =O in their structures which are available for the interaction with the mild steel surface. The interaction of these constituents with the mild steel surface takes place via the -OR_3 groups and >NH groups which makes it an efficient inhibitor.

Figure 4.62

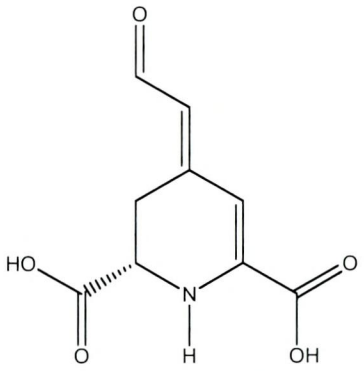
Structure of phytoconstituents of *Mirabilis jalapa*



a) Betacyanin



b) Betaxanthin



c) Betalamic acid

The adsorption isotherms obtained for the dissolution of mild steel in 1M HCl and in 0.5M H_2SO_4 suggest that adsorption of the inhibitors take place on the surface of mild steel. The FTIR studies suggest that the adsorption takes place via the heteroatoms present in the constituent molecules of the inhibitor in both 1M HCl and 0.5M H_2SO_4 media.

4.10 Effectiveness of the Pickling bath

Inorder to find out the effectiveness of the pickling bath, experiment was conducted by immersing different sets of samples in triplicates for a period of 1 h in the same bath. After removing the first set of samples, a fresh set of samples were immersed in the bath. Likewise the experiment was repeated everytime with a fresh set of samples. The results are presented in table 4.49.

Table 4.49

Inhibition efficiency of the extracts in 1M HCl and 0.5M H_2SO_4 obtained during continuous monitoring of the pickling bath

Extract	1M HCl					0.5M H_2SO_4				
(5%v/v)	1 set	2 set	3 set	4 set	5 set	1 set	2 set	3 set	4 set	5 set
CFL	94.08	92.09	92.04	92.27	81.88	89.68	89.38	89.22	89.54	85.43
BSL	90.68	92.57	93.38	92.09	82.85	92.62	92.25	92.06	91.87	89.02
MJF	93.29	92.59	92.95	90.84	81.83	91.09	90.54	90.29	89.15	86.81

The results (Table 4.49) show that the 1M HCl bath was effective for 3 sets of samples and for the fourth set CFL was effective, whereas for BSL and MJF, there was a slight decrease in the efficiency. However for the fifth set, for all the extracts there was a large decrease in inhibition efficiency.

In case of 0.5M H_2SO_4 medium, the bath is effective for 3 sets of samples with CFL and BSL whereas for 1 set in MJF after which it decreased slightly for further sets of samples. From the fourth set the efficiency decreased for all the inhibitors.

This shows that all the phytochemical constituents were not completely utilized in the beginning of the immersion of the samples, ie., less number of inhibitor molecules were sufficient to cover the surface of mild steel. Hence the same pickling bath can be used again and again till all the phytochemical constituents are utilized to protect the mild steel surface, thereby minimizing the acid consumption. It was observed from the study that the same pickling bath can be used for number of sets before changing.

4.11 Durability and Stability test

To test the stability of the extract and the suitable storage condition, the prepared extract was divided into two portions and one portion was stored in laboratory condition and the other portion was refrigerated. The inhibition efficiency of the stored extracts were studied once in a week for 30 days and then monthly for eight months and is given in tables 4.50-4.52 for CFL, BSL and MJF respectively.

Table 4.50

Inhibition efficiency of CFL extract stored under different storage conditions for the dissolution of mild steel in 1M HCl

Conc of the extract (% v/v)		0.05	0.5	1.0	2.0	3.0	4.0	5.0
1st day		38.53	64.11	76.29	81.70	82.79	84.94	86.81
1 week	WR	21.12	25.63	26.33	36.12	39.79	53.51	54.91
	AR	**29.67**	**38.92**	**47.28**	**63.19**	**73.22**	**79.93**	**81.31**
2 week	WR	61.69	75.92	82.67	83.01	85.04	85.98	86.50
	AR	**32.55**	**46.03**	**51.29**	**62.82**	**69.77**	**73.14**	**79.45**
3 week	WR	64.80	76.71	79.33	81.85	84.37	86.01	87.60
	AR	**30.31**	**45.22**	**49.72**	**53.17**	**60.38**	**66.91**	**72.36**
1 month	WR	61.11	72.13	75.24	76.66	77.32	82.15	84.52
	AR	**30.42**	**41.63**	**47.21**	**48.76**	**54.84**	**63.29**	**69.94**
2 month	WR	36.38	43.59	46.39	49.80	57.02	60.25	67.21
	AR	**26.32**	**31.88**	**40.88**	**46.13**	**48.19**	**59.69**	**61.87**
3 month	WR	65.51	68.11	72.32	74.78	78.83	80.74	82.15
	AR	**49.73**	**55.42**	**62.85**	**70.96**	**73.55**	**79.42**	**81.43**
4 month	WR	62.29	76.86	79.94	84.49	85.53	88.06	88.72
	AR	**60.44**	**77.33**	**82.48**	**85.20**	**88.02**	**89.76**	**90.43**
5 month	WR	60.23	64.21	69.42	73.25	75.74	77.85	81.16
	AR	**54.23**	**75.19**	**80.83**	**83.21**	**85.38**	**89.05**	**89.97**
6 month	WR	23.19	64.03	76.52	82.36	83.82	86.12	87.66
	AR	**29.76**	**72.53**	**79.74**	**80.48**	**83.62**	**87.20**	**88.59**
7 month	WR	33.24	41.96	47.35	53.86	66.02	71.49	76.93
	AR	**30.38**	**69.08**	**75.62**	**78.29**	**80.41**	**83.93**	**85.31**
8 month	WR	35.92	42.34	48.95	52.78	64.83	73.72	78.37
	AR	**32.94**	**63.27**	**69.43**	**74.06**	**78.63**	**79.66**	**81.28**

WR- Without Refrigeration, AR- After Refrigeration

Table 4.51

Inhibition efficiency of BSL extract stored under different storage conditions for the dissolution of mild steel in 1M HCl

Conc of the extract (% v/v)		0.05	0.5	1.0	2.0	3.0	4.0	5.0
1st day		29.04	31.72	35.32	39.10	49.90	57.73	60.57
1 week	WR	45.16	69.82	74.47	81.02	84.46	88.53	89.16
	AR	**22.35**	**24.56**	**37.68**	**54.21**	**65.81**	**70.56**	**77.93**
2 week	WR	2.81	39.10	42.35	53.54	57.42	63.23	66.53
	AR	**13.88**	**33.17**	**42.55**	**57.92**	**60.62**	**65.59**	**70.96**
3 week	WR	2.06	23.54	26.73	33.15	46.66	47.04	54.43
	AR	**12.67**	**38.48**	**43.61**	**55.23**	**61.29**	**63.33**	**68.93**
1 month	WR	77.25	81.79	83.06	85.16	87.11	86.85	89.02
	AR	**15.22**	**42.87**	**42.96**	**56.03**	**60.74**	**61.59**	**64.87**
2 month	WR	5.16	27.81	35.11	42.68	48.02	47.05	53.09
	AR	**19.56**	**48.84**	**42.72**	**56.87**	**59.8**	**59.09**	**62.55**
3 month	WR	2.96	19.09	21.83	35.22	28.85	38.67	43.01
	AR	**32.05**	**53.48**	**65.91**	**71.53**	**75.21**	**78.36**	**80.32**
4 month	WR	65.88	62.23	77.2	81.46	83.60	86.28	86.44
	AR	**65.81**	**64.30**	**78.9**	**84.82**	**87.64**	**89.02**	**89.96**
5 month	WR	60.59	72.77	71.70	83.55	86.64	88.27	88.96
	AR	**52.31**	**60.02**	**72.19**	**77.83**	**82.56**	**84.11**	**85.44**
6 month	WR	35.79	57.79	66.01	72.90	74.18	77.67	80.22
	AR	**20.75**	**57.50**	**64.64**	**70.98**	**75.10**	**78.51**	**78.30**
7 month	WR	5.97	23.45	30.49	34.72	44.05	46.28	51.95
	AR	**19.65**	**52.93**	**59.80**	**72.18**	**79.45**	**81.29**	**83.49**
8 month	WR	36.82	62.69	52.38	79.24	82.46	85.05	87.22
	AR	**19.18**	**33.84**	**54.38**	**76.59**	**82.22**	**85.69**	**88.89**

Table 4.52

Inhibition efficiency of MJF extract stored under different storage conditions for the dissolution of mild steel in 1M HCl

Conc of the extract (% v/v)		0.05	0.5	1.0	2.0	3.0	4.0	5.0
1st day		42.49	58.09	59.66	62.11	68.39	73.11	75.21
1 week	WR	38.26	59.15	63.10	68.64	71.55	75.53	77.75
	AR	**25.57**	**47.39**	**54.12**	**60.82**	**64.33**	**72.36**	**74.29**
2 week	WR	12.17	27.60	44.06	49.63	56.54	63.71	65.23
	AR	**18.37**	**31.93**	**46.22**	**51.90**	**55.32**	**64.84**	**67.91**
3 week	WR	5.45	26.79	35.35	44.87	50.50	55.84	60.76
	AR	**9.87**	**23.47**	**34.02**	**42.95**	**51.94**	**59.49**	**61.67**
1 month	WR	8.89	55.89	59.93	69.42	76.92	81.51	83.39
	AR	**15.43**	**32.87**	**46.29**	**54.55**	**59.13**	**65.34**	**77.42**
2 month	WR	34.67	40.16	44.16	46.79	57.58	62.33	63.97
	AR	**42.26**	**44.26**	**55.12**	**62.12**	**65.51**	**75.24**	**81.32**
3 month	WR	9.54	23.0	24.36	34.02	38.24	35.65	38.15
	AR	**54.67**	**60.22**	**68.95**	**70.19**	**74.23**	**81.04**	**82.98**
4 month	WR	69.46	77.40	82.15	84.50	86.25	87.28	89.32
	AR	**64.41**	**74.54**	**82.15**	**84.81**	**85.61**	**88.23**	**89.00**
5 month	WR	64.21	68.06	71.98	80.82	81.74	82.67	84.12
	AR	**60.72**	**69.23**	**80.18**	**81.98**	**88.03**	**86.79**	**87.38**
6 month	WR	61.62	72.24	78.87	81.32	82.05	83.23	84.43
	AR	**59.64**	**68.73**	**77.94**	**80.19**	**83.27**	**86.11**	**87.59**
7 month	WR	12.74	23.45	30.49	34.72	44.05	46.28	51.95
	AR	**43.72**	**55.34**	**64.92**	**74.56**	**76.54**	**79.04**	**81.44**
8 month	WR	15.52	25.76	35.79	41.52	48.05	52.38	54.74
	AR	**31.29**	**47.56**	**55.37**	**62.83**	**68.96**	**74.28**	**77.30**

It is observed from table 4.50-4.52 that there is no regular trend in the inhibition efficiency of the extracts stored in table condition studied at different period of storage. This may be due to the variation in the composition of the constituents in

the extract during storage. The variation may be due to the settling of either one or more of the constituents or due to the decomposition of any of the constituents.

From the tables, it is clear that the inhibition efficiencies of the extracts stored without refrigeration and in refrigerated condition are comparable. This shows that the extract need not be stored in refrigerator, as it is effective in the table condition itself.

Table 4.53

Inhibition efficiency of CFL extract stored under different storage conditions for the dissolution of mild steel in 0.5 M H_2SO_4

Conc of the extract (% v/v)		0.05	0.5	1.0	2.0	3.0	4.0	5.0
1st day		12.48	16.93	17.76	21.67	32.78	33.79	34.41
1 week	WR	31.36	75.09	81.8	84.45	87.48	88.34	89.72
	AR	**18.42**	**32.66**	**44.93**	**56.82**	**68.49**	**72.53**	**80.41**
2 week	WR	34.87	76.80	81.85	86.75	88.87	89.66	91.96
	AR	**21.34**	**39.42**	**52.43**	**61.71**	**72.41**	**79.36**	**82.32**
3 week	WR	23.38	54.57	69.87	71.31	81.35	83.21	84.61
	AR	**32.18**	**43.44**	**59.38**	**67.34**	**78.43**	**81.13**	**84.11**
1 month	WR	26.52	57.83	64.37	69.22	81.93	84.03	84.36
	AR	**38.62**	**49.31**	**60.23**	**66.23**	**72.16**	**74.91**	**82.19**
2 month	WR	37.60	64.07	74.55	78.43	82.54	84.85	86.59
	AR	**44.08**	**52.41**	**58.85**	**64.11**	**67.49**	**70.11**	**71.17**
3 month	WR	21.3	34.54	63.11	76.01	81.74	82.81	85.27
	AR	**31.36**	**49.14**	**61.56**	**66.52**	**71.53**	**75.16**	**79.73**
4 month	WR	9.34	32.81	64.67	71.63	72.29	74.41	81.48
	AR	**12.43**	**46.09**	**63.91**	**73.93**	**78.30**	**82.86**	**86.05**
5 month	WR	18.03	44.01	63.54	71.71	78.74	82.0	85.34
	AR	**14.21**	**39.16**	**60.03**	**71.59**	**76.66**	**81.92**	**84.97**
6 month	WR	8.10	50.95	61.23	69.30	77.10	79.55	82.38
	AR	**15.91**	**34.93**	**61.05**	**70.50**	**76.46**	**81.40**	**84.20**
7 month	WR	9.43	34.98	45.86	56.53	64.91	71.39	76.37
	AR	**14.23**	**33.14**	**59.17**	**68.23**	**73.44**	**80.19**	**82.93**
8 month	WR	11.43	23.21	35.47	44.93	60.82	67.45	78.28
	AR	**14.56**	**32.19**	**57.03**	**64.38**	**70.36**	**78.37**	**82.01**

Table 4.54

Inhibition efficiency of BSL extract stored under different storage conditions for the dissolution of mild steel in 0.5 M H_2SO_4

Conc of the extract (% v/v)		0.05	0.5	1.0	2.0	3.0	4.0	5.0
1st day		20.85	40.22	58.70	61.77	67.52	69.15	73.03
1 week	WR	21.28	45.83	62.98	75.43	87.42	88.81	88.98
	AR	**16.42**	**42.19**	**59.33**	**60.69**	**68.51**	**72.43**	**77.96**
2 week	WR	24.77	56.29	68.49	79.65	85.62	87.21	88.66
	AR	**17.31**	**45.26**	**63.41**	**68.33**	**72.94**	**79.14**	**85.21**
3 week	WR	23.19	64.03	76.52	82.36	83.82	86.12	88.26
	AR	**20.43**	**47.93**	**68.24**	**73.58**	**78.62**	**83.11**	**86.42**
1 month	WR	2.41	33.57	36.36	45.97	49.29	54.28	57.11
	AR	**21.34**	**52.62**	**69.13**	**72.91**	**79.96**	**82.03**	**85.14**
2 month	WR	22.31	71.95	77.00	84.35	91.43	89.55	90.24
	AR	**19.48**	**56.25**	**69.54**	**73.83**	**81.59**	**82.59**	**84.30**
3 month	WR	29.73	68.46	74.26	80.26	82.99	85.26	86.72
	AR	**23.29**	**61.24**	**71.62**	**79.45**	**83.63**	**85.55**	**86.03**
4 month	WR	29.71	60.67	70.21	76.16	81.19	85.24	87.32
	AR	**27.34**	**70.05**	**78.98**	**84.63**	**87.79**	**88.24**	**88.69**
5 month	WR	27.89	58.52	70.20	77.74	83.22	84.98	86.63
	AR	**43.21**	**76.39**	**81.43**	**87.62**	**90.04**	**91.44**	**92.69**
6 month	WR	59.09	68.64	79.81	85.31	86.27	88.63	88.70
	AR	**75.88**	**87.54**	**90.46**	**92.97**	**93.59**	**94.41**	**95.41**
7 month	WR	15.46	24.89	50.81	70.30	76.78	81.07	82.14
	AR	**73.29**	**82.63**	**88.56**	**90.12**	**91.43**	**92.97**	**94.11**
8 month	WR	6.41	23.45	30.49	34.72	44.05	46.28	51.95
	AR	**70.23**	**79.41**	**87.59**	**89.92**	**90.03**	**91.46**	**92.44**

Table 4.55

Inhibition efficiency of MJF extract stored under different storage conditions for the dissolution of mild steel in 0.5 M H_2SO_4

Conc of the extract (% v/v)		0.05	0.5	1.0	2.0	3.0	4.0	5.0
1st day		38.45	63.35	72.82	79.90	82.39	83.46	83.56
1 week	WR	27.60	44.06	49.63	56.97	68.42	70.62	74.26
	AR	**31.26**	**56.89**	**63.22**	**71.52**	**79.43**	**80.76**	**81.32**
2 week	WR	22.43	60.97	65.37	70.79	69.09	71.17	76.11
	AR	**28.59**	**54.27**	**60.87**	**68.43**	**73.66**	**78.29**	**80.76**
3 week	WR	18.51	60.33	62.53	69.07	70.14	74.52	75.62
	AR	**25.03**	**42.18**	**59.33**	**65.28**	**71.34**	**76.53**	**78.29**
1 month	WR	2.81	39.10	42.35	53.54	57.42	63.23	66.53
	AR	**27.07**	**41.88**	**62.71**	**67.92**	**71.20**	**76.04**	**79.38**
2 month	WR	8.88	55.88	59.93	69.42	76.91	77.42	81.50
	AR	**30.93**	**41.56**	**65.15**	**70.06**	**72.40**	**74.99**	**79.16**
3 month	WR	15.62	33.98	39.57	44.80	49.08	52.31	55.21
	AR	**32.59**	**49.62**	**71.96**	**78.25**	**79.57**	**81.34**	**83.29**
4 month	WR	32.70	55.83	68.51	72.12	77.69	79.54	83.12
	AR	**38.53**	**64.11**	**76.29**	**81.7**	**82.79**	**84.94**	**86.81**
5 month	WR	23.89	56.23	67.49	73.42	78.23	80.47	82.96
	AR	**35.36**	**63.92**	**74.29**	**79.53**	**82.03**	**83.96**	**86.01**
6 month	WR	18.5	52.8	65.72	74.0	78.86	81.58	82.75
	AR	**32.44**	**60.13**	**71.29**	**79.24**	**81.79**	**83.55**	**85.01**
7 month	WR	18.52	53.59	72.39	77.05	82.88	85.48	88.26
	AR	**29.23**	**46.52**	**64.81**	**73.23**	**78.52**	**82.13**	**84.16**
8 month	WR	25.77	38.35	53.01	74.31	79.18	84.23	86.90
	AR	**25.51**	**32.94**	**56.01**	**69.50**	**74.42**	**80.56**	**82.13**

With increase in concentration of the inhibitor, the inhibition efficiency has increased at all the different course of time. There is no regular trend of decrease or increase in efficiency with storage time. At the maximum concentration 5% v/v, there

is no significant reduction in the efficiency which shows that the extract can be stored for a longer time. The performance of the inhibitor is better in the one stored under laboratory conditions. Hence the inhibitor can be used for six months storing it under laboratory conditions.

4.12 Petroleum ether washed extract

A pilot study was conducted with the extracts prepared from the leaves/flowers after washing with petroleum ether at 1h and 3h immersion period. The inhibition efficiencies obtained are presented in table 4.56 and 4.57 for 1M HCl and 0.5M H_2SO_4.

Table 4.56

Variation of inhibition efficiency for the mild steel corrosion in 1M HCl in presence of different concentrations of the extract prepared after washing with petroleum ether with immersion period at 303 ± 2 K.

Conc of the extract (% v/v)	Percentage inhibition efficiency					
	CFL		BSL		MJF	
	1h	3h	1h	3h	1h	3h
0.05	15	22	14	23	20	27
0.50	24	36	22	34	28	31
1.00	35	47	35	41	36	40
2.00	42	60	46	50	45	49
3.00	56	68	58	62	57	61
4.00	63	71	64	73	68	70
5.00	69	73	72	80	71	74

Table 4.57

Variation of inhibition efficiency for the mild steel corrosion in 0.5M H_2SO_4 in presence of different concentrations of the extract prepared after washing with petroleum ether with immersion period at 303 ± 2 K.

Conc of the extract (% v/v)	Percentage inhibition efficiency					
	CFL		BSL		MJF	
	1h	3h	1h	3h	1h	3h
0.05	10	28	18	25	14	25
0.50	14	32	23	39	19	31
1.00	16	41	34	47	28	40
2.00	21	48	44	52	36	51
3.00	27	55	56	69	47	62
4.00	38	67	67	74	55	72
5.00	52	70	74	82	63	79

It is evident from tables 4.56 and 4.57 that the extract prepared after washing with petroleum ether has inhibition efficiency less than that of the inhibition efficiency of the extract prepared without washing with petroleum ether. The maximum efficiency obtained was 80% with 5% v/v concentration of BSL extract at 3 h in HCl. In H_2SO_4 medium the maximum efficiency was 82% (5% v/v at 3 h). This efficiency does not approach the prescribed efficiency for pickling inhibitors. Also usage of petroleum ether will be more expensive and time consuming.

4.13 Extract prepared by soaking the plant materials for 12 hours

A trial has been made to reduce the cost as well as the time consumed in the preparation of the extract (without refluxing). The dried leaves and flowers were kept immersed in acid solutions for 12 hours and then filtered. This was used as the stock solution. The immersion studies were carried out with different concentrations of the extracts prepared from the stock solution for a period of 1h and 3h at 303 ± 2 K. The inhibition efficiency is given in table 4.58 and 4.59 for 1M HCl and 0.5M H_2SO_4.

Table 4.58

Variation of inhibition efficiency for the mild steel corrosion in 1M HCl in presence of different concentrations of the extracts (prepared without refluxing)

Conc of the extract (% v/v)	Percentage inhibition efficiency					
	CFL		BSL		MJF	
	1h	3h	1h	3h	1h	3h
0.05	44	51	47	54	39	48
0.50	48	57	55	62	43	51
1.00	61	68	62	69	49	56
2.00	69	74	71	73	56	63
3.00	76	79	74	79	64	71
4.00	81	82	77	84	72	78
5.00	82	84	81	89	80	85

Table 4.59

Variation of inhibition efficiency for the mild steel corrosion in 0.5M H_2SO_4 in presence of different concentrations of the extracts (prepared without refluxing)

Conc of the extract (% v/v)	Percentage inhibition efficiency					
	CFL		BSL		MJF	
	1h	3h	1h	3h	1h	3h
0.05	19	28	29	40	26	39
0.50	31	46	58	65	42	53
1.00	50	61	68	73	51	60
2.00	64	72	70	79	59	68
3.00	69	78	76	82	72	79
4.00	75	83	81	85	79	81
5.00	78	87	83	89	81	86

From the tables 4.58 and 4.59, it is seen that the extracts proved as good inhibitors. The inhibition efficiency increased with increase in concentration of the extract and with increase in the immersion period. The maximum efficiency (84% in CFL, 89% in BSL and 85% in MJF) was obtained at 3 h immersion period and at 5%

v/v concentration of the extracts. At 5% v/v concentration of the extracts, the maximum efficiencies obtained were above 80% in all the extracts in the studied immersion period except for CFL in 0.5M H_2SO_4 at 1h (78%). The best efficiency (89%) is obtained for BSL in both acid media, which is within the prescribed efficiency limit ie, 87% for acid pickling inhibitors (**Popova, 2007).** Further increase in the efficiency may be obtained by increasing the soaking time of the leaves in acid, by which the extract in bulk may be prepared in the pickling bath itself without carrying out the refluxing process. Hence this becomes an industrial-friendly method for the preparation of the inhibitor.

4.14 Bioaccumulation: (UV-Visible absorption spectroscopic technique)

Green chemistry or pollution prevention at molecular level, is chemistry designed to reduce or eliminate the use or generation of hazardous material associated with manufacture and application of chemicals. As a stringent requirement for the protection of environment, the chemicals are allowed to use as inhibitors with three main criteria- their level of biodegradability, bioaccumulation and toxicity. An ideal green corrosion inhibitor according to the Paris Commission (PARCOM) is non-toxic, readily biodegradable and shows no bioaccumulation **(Schmitt and Sale, 2000).**

A typical green corrosion inhibitor requires standardization of environmental testing for partition coefficient (bioaccumulation). Bioaccumulation means an increase in the concentration of a chemical in biological organism over a time compared to the chemical concentration in the environment.

Bioaccumulation provides a measure of the distribution of the inhibitor between octanol and water mixture and expressed as logarithm of the octanol/water partition co-efficient (log P_o/w) and it must be below 3 for a typical green corrosion inhibitor **(Shaheen Taj *et al.*, 2006)**. For preliminary investigation, a simpler method of using UV-visible spectroscopy was used to evaluate log P_o/w.

To find out the bioaccumulation of the selected inhibitors CFL, BSL and MJF, the samples of analytes were prepared, shaken vigorously in n-octanol and water. After shaking the octanol layers were sampled and the quantity of inhibitors in octanol and water were estimated by measuring absorbance using PC based double beam UV-visible spectrophotometer (Systronics-2202).

Table 4.60

Concentration of the inhibitor, octanol and phosphate buffer

Composition	Volume in ml		
	n-octanol	Inhibitor	Buffer
C-1	5.0	2.0	5
C-2	5.8	2.2	4
C-3	6.6	2.4	3
C-4	7.2	2.8	2
C-5	8.4	2.6	1

Table 4.60 gives the composition of prepared mixture containing n-octanol, inhibitors-CFL, BSL and MJF and aqueous phosphate buffer.

If B is the absorbance of octanol layer and A is the absorbance of the octanol layer after the addition of phosphate buffer then the concentration of the plant extracts present in the octanol layer, $C_{octanol}$ is proportional to B and concentration of the plant extract present in aqueous phase, $C_{aqueous}$ is proportional to (B-A).

The partition co-efficient P_o/w is defined as the ratio of the concentration of plant extract present in the octanol layer $C_{octanol}$ to the concentration of the plant extract present in the aqueous layer $C_{aqueous}$.

$$\mathbf{P_o/w = C_{octanol}/C_{aqueous} = B/B\text{-}A}$$

According to the Paris Commission (PARCOM) one of the criteria for the inhibitor to be environmentally acceptable it shouldn't show any bioaccumulation and the value of log $P_o/w < 3$ indicates low bioaccumulation.

Table 4.61

Partition co-efficient values for CFL, BSL and MJF in octanol-water system

Inhibitor	Composition	Wave length (nm)	B	Wave length (nm)	A	P_o/w	log P_o/w	log P_o/w
CFL	C-1	230	1.447	350	1.239	6.96	0.84	<3
	C-2	230	1.506	210	1.450	26.89	1.43	<3
	C-3	230	1.511	250	1.432	19.13	1.28	<3
	C-4	230	1.575	250	1.397	8.85	0.95	<3
	C-5	230	1.441	350	1.293	9.74	0.99	<3
BSL	C-1	230	1.509	210	1.345	9.20	0.96	<3
	C-2	230	1.360	250	1.212	9.19	0.96	<3
	C-3	230	1.336	250	1.123	6.27	0.80	<3
	C-4	230	1.360	250	1.269	14.95	1.17	<3
	C-5	230	1.237	250	1.163	16.72	1.22	<3
MJF	C-1	230	0.723	250	0.471	2.87	0.46	<3
	C-2	230	0.665	250	0.422	2.74	0.44	<3
	C-3	230	0.710	250	0.515	3.64	0.56	<3
	C-4	230	0.690	250	0.492	3.48	0.54	<3
	C-5	230	0.646	250	0.554	7.02	0.85	<3

The absorbance and log P_o/w values are shown in table 4.61. For the inhibitors CFL, BSL and MJF the values of log P_o/w are found to be less than 3 indicating that these extracts exhibit low bioaccumulation in accordance with the environmental regulations for green inhibitors.

4.15 Industrial Field Testing

The real fruit of any research can be tasted only if it is applied in practice. In that way, this study has been extended to test the applicability of the extracts as inhibitors in small scale industries.

Due to the restrictions of the pollution control board, electroplating industries find difficulty in the disposal of waste. Efforts have been taken to develop eco-friendly and biodegradable material as inhibitors for the pickling process in electroplating industries. Hence the extracts were tested under industrial conditions, ie, the samples and acids used in the industry were taken for testing. The samples in triplicates were immersed in acid in the absence and in presence of the extracts.

In one industry selected for the study, H_2SO_4 is used for pickling. The time of immersion is 1 h. After the immersion the samples are washed with water and dried.

In other industry, HCl is used as pickling acid. The time of immersion is 20 minutes. After the immersion the samples are washed with water and immediately electroplated.

Similar procedure was adopted to test the extracts. During the immersion period, the acid baths were noted for the mist formation, hydrogen evolution and formation of residue. It was observed that there is no mist formation, reduced hydrogen evolution and no residue in H_2SO_4 bath. The visual observation of the samples after removal from the acid baths does not show any difference. From each set of triplicates immersed, one sample was electroplated and the other two were left in the industrial environment. The electroplated sample was tested for the thickness. The thickness was also not affected by the usage of extract as inhibitor.

The photographs of pickling baths and electro plating bath are given in plates 1.1, 1.2 & 1.3. Fresh industrial samples, samples immersed in H_2SO_4 bath, samples after pickling and pickled samples after one week are shown in plates 2.1, 2.2, 2.3 & 2.4 respectively.

Fresh industrial samples, samples immersed in HCl bath, samples after pickling and pickled samples after one week are shown in plates 3.1, 3.2, 3.3 & 3.4 respectively.

In another set, the acid used in the industry was taken to the lab and triplicates of the mild steel sample and one industrial sample were tested for weight loss in the absence and in presence of 5% v/v extract for the same duration of immersion as in industry. The same pickling baths were used for the second time and the inhibition efficiency was calculated. The efficiency of the inhibitors in the industrial acid baths is given in the table 4.60. These samples were left in lab environment for 1 week and then photographed.

Plates 4.1, 4.2, 4.3 & 4.4 shows the samples immersed in sulphuric acid bath, samples after pickling, pickled samples after one week and electro plated samples.

Plates 5.1, 5.2, 5.3 & 5.4 shows the samples immersed in HCl bath, samples after pickling, pickled samples after one week and electro plated samples.

Table 4.62

Inhibition efficiencies obtained by Weight loss method with the industrial acids for the set of lab and industrial samples

Extract (5% v/v)	H_2SO_4 (% IE) Lab sample/Industrial sample		HCl (% IE) Lab sample/Industrial sample	
	1 set	2 set	1 set	2 set
CFL	58/21	54/20	40/16	37/15
BSL	84/50	80/46	61/50	23/49
MJF	70/47	68/44	47/47	39/38

From the table, it is evident that the inhibition efficiency for the industrial samples is less when compared with lab samples. The efficiency for the industrial sample may be increased by increasing the concentration of the extract or the pickling time.

The following were the conclusions from the field study

- All the studied extracts behaved as good pickling inhibitors
- There was reduction in the hydrogen evolution and acid mist formation
- The pickling time was almost the same for HCl without and in presence of the extracts, whereas in H_2SO_4 with extract the pickling time required was nearly two times than the acid without extract
- The presence of extract did not cause any difference in the thickness of the plated samples
- No residue was seen in H_2SO_4 bath

Presence of the extract reduced the fumes and does not affect the plating efficiency. Hence the extracts of *Cassia fistula* leaves, *Bougainvillea spectabilis* leaves and *Mirabilis jalapa* flowers may be recommended as pickling inhibitors in the industries.

PLATE 1

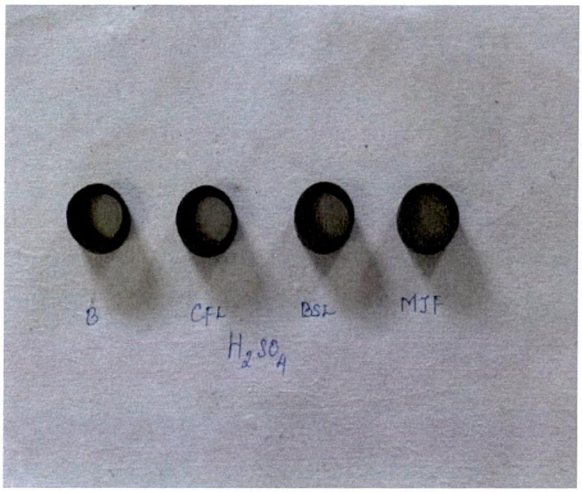
1.1 SULPHURIC ACID PICKLING BATHS

1.2 HYDROCHLORIC ACID PICKLING BATH

1.3 ELECTRO PLATING BATH

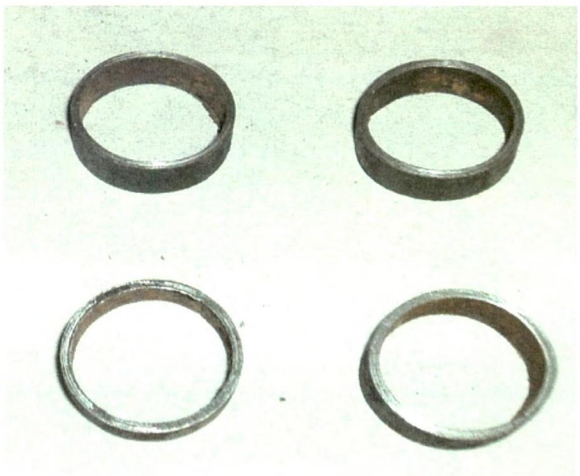
PLATE 2

2.1 FRESH SAMPLES



2.2 SAMPLES IMMERSED IN ACID BATH (H_2SO_4)

2.3 SAMPLES AFTER PICKLING



2.4 PICKLED SAMPLES AFTER ONE WEEK

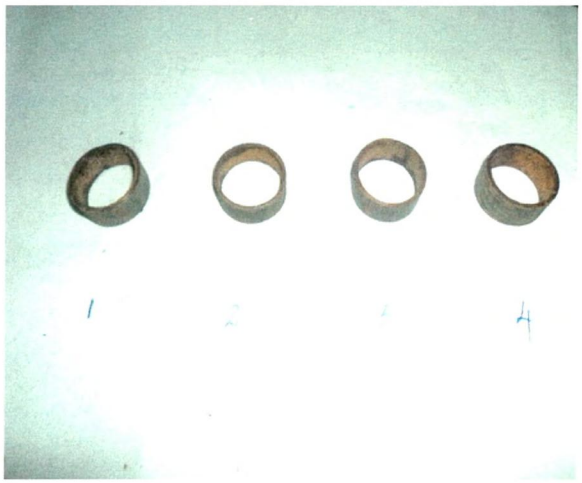
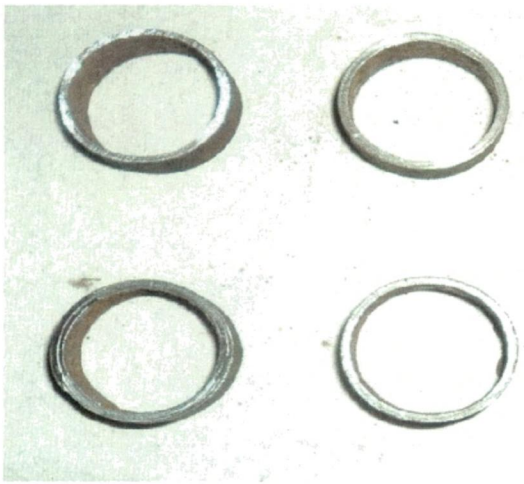


PLATE 3

3.1 FRESH SAMPLES

3.2 SAMPLES IMMERSED IN ACID BATH (HCl)

3.3 SAMPLES AFTER PICKLING



3.4 PICKLED SAMPLES AFTER ONE WEEK

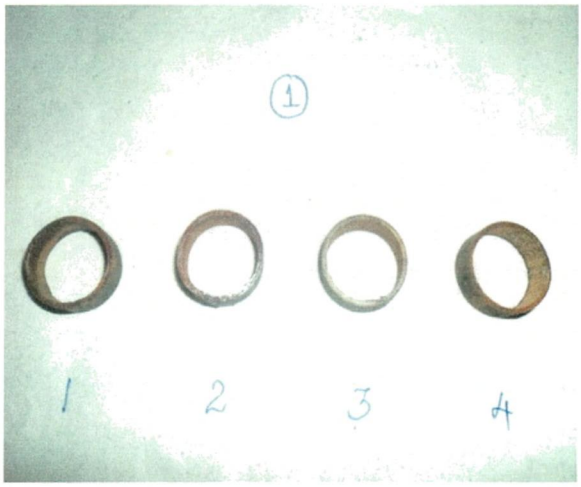
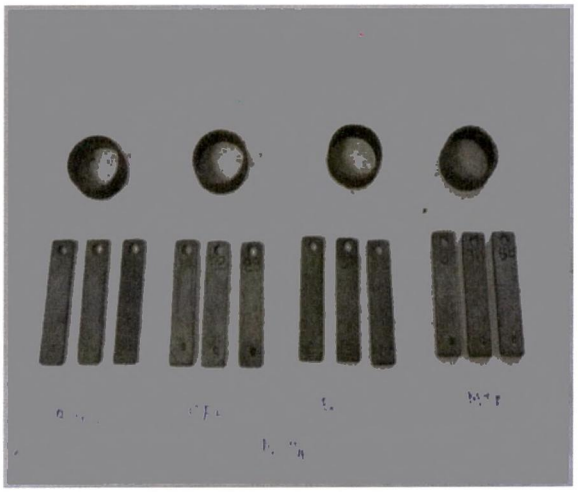


PLATE 4

4.1 SAMPLES IMMERSED IN INDUSTRIAL ACID (H_2SO_4)

4.2 SAMPLES AFTER PICKLING UNDER LAB CONDITIONS



4.3 PICKLED SAMPLES AFTER ONE WEEK

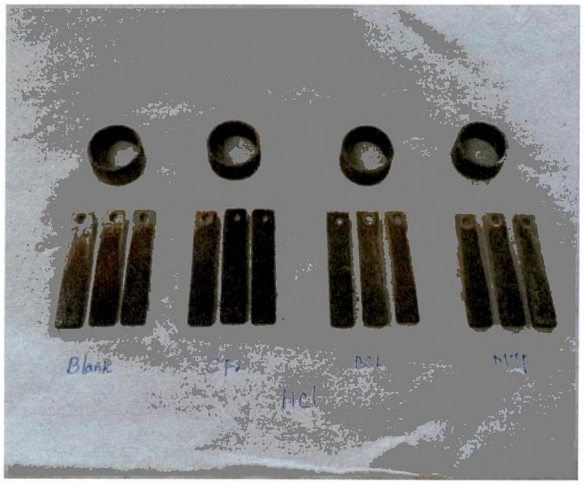
4.4 ELECTRO PLATED SAMPLES

PLATE 5

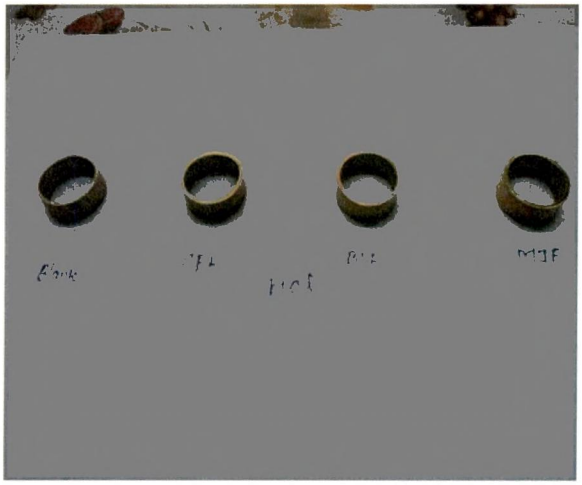
5.1 SAMPLES IMMERSED IN INDUSTRIAL ACID (HCl)

5.2 SAMPLES AFTER PICKLING UNDER LAB CONDITIONS

5.3 PICKLED SAMPLES AFTER ONE WEEK



5.4 ELECTRO PLATED SAMPLES



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Ref.

Date :12.02.2011...

TO WHOMSOEVER IT MAY CONCERN

This is to certify that Mrs.P.Thilagavathy, Ph.D., scholar from Avinashilingam Deemed University has tested her inhibitors in our industry for the corrosion inhibition.

When the plant extracts (Cassia fistula leaves, Bougainvillea spectabilis leaves and Mirabilis jalapa flowers) were added to the pickling acid, the acid mist and the residue formation was reduced considerably. It was noted that there was no change in the quality of the samples pickled using the acid with inhibitors and without inhibitors. We observed that the pickling time was increased when the plant extracts were added to the acid bath.

Her effort to find eco-friendly inhibitors for pickling is appreciated. We suggest that the plant extracts (Cassia fistula leaves, Bougainvillea spectabilis leaves and Mirabilis jalapa flowers) may be used as pickling inhibitors.

For Vinayaka Bright Industries

Partner

Partner

TOUCHWELL INDUSTRY

DIFFERENTIATE OF SURFACE FINISHING

Date: 25.02.11

TO WHOMSOEVER IT MAY CONCERN

This is to inform that Mrs.P.Thilagavathy, Ph.D., scholar from Avinashilingam Deemed University has tested her inhibitors in our plating industry for the corrosion inhibition effectiveness.

We have observed that all the three inhibitors tried by her worked effectively in the industrial acid. It was noted that no fumes arise during pickling process. The electroplated samples after pickling using the acid with inhibitors was similar to the other samples pickled in acid without inhibitors.

We appreciate her effort to find eco-friendly and economical inhibitors for pickling process. I suggest that the plant extracts (Cassia fistula leaves, Bougainvillea spectabilis leaves and Mirabilis jalapa flowers) may be used as pickling inhibitors.

For TOUCHWELL INDUSTRY

Proprietor

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