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COMPARISON OF CORROSION MITIGATION EFFICIENCY OF SEED COAT OF *COFFEA ARABICA* FOR MILD STEEL IN 1 M HCl AND 0.5 M H_2SO_4

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The protection efficiency of seed coat of *Coffea Arabica* fruit extract on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 were evaluated by using Gravimetric method. The study was carried out by varying the parameters like inhibitor concentration, immersion period and temperature. The maximum efficiency was obtained at 2.5 %(v/v) concentration of the inhibitor in both 1 M HCl and 0.5 M H_2SO_4. The protective action of the acid extract was maximum at 12 h in both 1M HCl and 0.5 M H_2SO_4. In the temperature study the maximum efficiency was obtained at 333 K in 1M HCl and at 323 K in 0.5 M H_2SO_4.

KEYWORDS : *Coffea Arabica,* corrosion protection.

INTRODUCTION

Acid solutions are widely used in industries, the most important area of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. HCl and H_2SO_4 are widely used in the pickling processes of metals.

Mild steel is a very prominent material of construction and frequently comes in contact with aqueous solution which may be acidic in nature, or as a part of industrial process. But its susceptibility to rusting in humid air and its very high dissolution rate in acidic medium are the major obstacles in its use on a large scale. Hence the study of corrosion inhibition of Mild steel in aqueous aggressive media is very important.[1]

Use of inhibitors is a simple approach to give effective corrosion control.[2] Corrosion inhibitors reduce or prevent these reactions, they are adsorbed onto the metal surface and act by forming a barrier to oxygen and moisture, by complexing with metal ions or by removing corrodants from the environment, some of the inhibitors facilitate formation of passivating film on the metal surface. Unfortunately, most of the corrosion inhibitors are expensive and are synthetic chemicals having hazardous properties to living creatures and environment. So, it is very essential to choose cost effective and safely handled compounds to be used as corrosion inhibitors. In recent days many ecofriendly green inhibitors have been used. The acid extracts of *Occium viridis* [3], *Mentha pulegium* [4], *Nypafructicans wurmb* [5], *Lawsonia inermis* [6], *Hibiscus subdarifa* [7] , *Solanum verbasifolium* [8], *Michelia champaca*

[9], *Zenthoxylum alatum* [10] ,*Eugenia jambolans* [11], Leaves of *Occimum viridis, Telferia occidentalis, Azadirachta indica,* and seeds of *Garcinia kola* [12], Leaves and seeds of *Phyllanthus amarus* [13], *Ipomoea carnea* [14], Stem bark, leaves and fruits of *Proscopic cineraria,* [15] *Musa species peel* [16], *Cymbopogon proximus, Nigella sativa and Phaseolus vulgaris L*[17] were used as inhibitors for the corrosion of Mild steel in acidic media. The present study involves use of naturally occurring biodegradable material as the corrosion inhibitor.

EXPERIMENTAL METHODS

WEIGHT LOSS METHOD

Weight loss experiments were performed with mild steel specimen of size $5 \times 1 \text{ cm}^2$. The samples were polished with 280 grade emery paper, cleaned thoroughly with soap water, rinsed with distilled water, dried using filter paper and kept in a dessicator for further study. The elemental analysis was carried out using vacuum emission spectrometer Dv-4 and the mild steel used for the present study was found to contain Carbon-0.049%, Manganese-0.346%, Silicon-0.026%, Phosphorous – 0.038%, Sulphur – 0.020%, Chromium – 0.050%, Molybdenum – 0.019%, Nickel – 0.019% and Iron – 99.452%.

The weighed mild steel specimens in triplicate were immersed in 100 mL solutions in absence and in presence of various concentrations of the extract (acid extract of seed coat of *Coffea arabica*), at different immersion time and at different temperatures. Then the specimens were removed and dipped in sodium bicarbonate solution to remove the residual acid from the surface of the metal, washed with distilled water, dried with filter paper and reweighed. Denver M 220 D digital balance was used for weighing the specimens before and after immersion in various environments.

MEDIUM

Commercial grade HCl and H_2SO_4 were used for preparing solutions. Distilled water was used to prepare 1 M HCl and 0.5M H_2SO_4.

INHIBITOR

The *Coffea Arabica* fruit shell agrowaste (CAF) was collected from Mukkimalai village in Nilgiri hills, shadow dried and powdered. The extract was prepared by refluxing 25 grams of the powdered sample in 500 mL of 1 M HCl for 3 hours, kept overnight and then filtered and made upto the same volume using the same acid. The extract of CAF in 500 ml of 0.5 M H_2SO_4 was also prepared by the same procedure. This solution was taken as the stock solution and required dilutions were made from this solution.

ADSORPTION ISOTHERMS

When the inhibitor is present in the corroding solution, it is believed that inhibitor is adsorbed on the surface. An adsorption isotherm gives the relation between the coverage of an interface with the adsorbed species (the amount adsorbed) and the concentration of the species in solution. Interpretation of the performance of the adsorbent type of the inhibitor can be evaluated by fitting the data in one of the known adsorption isotherms.

Langmuir isotherm — $\log(\theta/1-\theta)$ Vs $\log C$
Temkin isotherm — θ Vs $\log C$
Freundlich isotherm — $\log\theta$ Vs $\log C$
Frumkin isotherm — $\log(\theta/1-\theta)/C$ Vs θ
Flory-Huggins isotherm — $\log(\theta/C)$ Vs $(1-\theta)$

RESULTS AND DISCUSSION

Weight loss method:

Effect of Inhibitor concentration

The effect of CAF on metal dissolution in 1 M HCl and 0.5 M H_2SO_4 at various concentrations has been studied and reported in Tables 1 & 2.

$$I\ E\% = \left[\frac{W_0 - W}{W_0}\right] \times 100$$

where W_0 and W are the corrosion rates of mild steel in 0.5 M H_2SO_4 in the absence and presence of definite concentrations of the inhibitor.

Table 1: Inhibition efficiencies of CAF on mild steel in 1 M HCl medium

S. No	Conc. v/v%	IE %					
		1 h	3 h	6 h	12 h	24 h	48 h
1	0.01	67.65	66.03	85.59	65.72	55.33	5.30
2	0.5	91.49	93.81	95.16	97.27	95.52	94.07
3	1	92.26	96.17	97.19	97.99	96.77	94.69
4	1.5	93.60	96.29	97.75	97.89	97.35	94.82
5	2	94.26	96.69	98.05	98.44	97.53	96.08
6	2.5	94.67	97.59	98.24	98.58	97.92	96.70

Table 2: Inhibition efficiencies of CAF on mild steel in 0.5 M H_2SO_4 medium

S. No	Conc. v/v%	IE %					
		1 h	3 h	6 h	12 h	24 h	48 h
1	0.01	55.89	64.62	64.91	55.42	14.45	0.05
2	0.5	82.37	92.50	93.92	92.98	89.59	82.05
3	1	85.19	92.52	95.00	94.55	91.52	86.69
4	1.5	86.21	92.42	95.44	95.15	92.26	88.07
5	2	87.76	95.79	95.48	95.43	94.09	89.38
6	2.5	85.42	95.43	96.06	96.51	94.58	89.54

The increase in inhibition efficiency with the increase in the concentration of the extracts was evident from the Inhibition efficiency values. The maximum efficiency of 98.58% was obtained for 2.5% (v/v) concentration of the inhibitor in 1 M HCl, whereas at the same concentration of the extract in 0.5 M H_2SO_4 the efficiency was found to be 96.51 %(v/v). This is quite evident from the comparative chart.

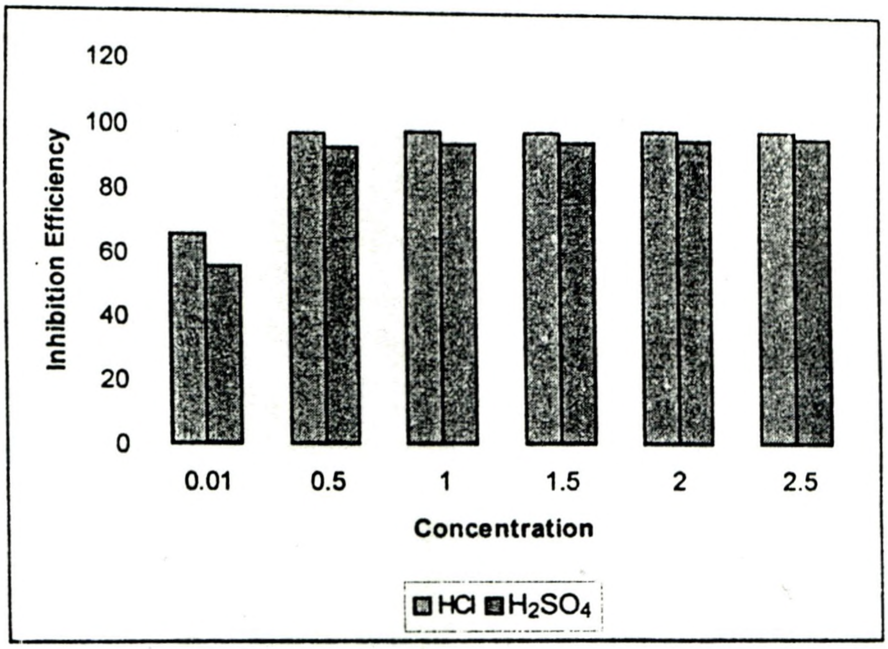

Fig. 1. Comparison of Inhibition efficiencies of CAF in 1M HCl and 0.5M H_2SO_4 for 12 h immersion period

Effect of period of immersion

To find out the optimum exposure time for maximum efficiency, Studies were carried out at various time intervals (1, 3, 6, 12, 24 and 48h) in the absence and presence of different concentrations of the inhibitor by Weight loss method. For all the immersion periods the I.E increased with increase in concentration of the inhibitor. The maximum efficiency was noted as 98.58% for 2.5% v/v of CAF extract in 1M HCl for 12 h and 96.51% for 2.5%v/v of CAF extract for 0.5 M H_2SO_4 in 12 h. Further increase in immersion time decreased the I.E in both the media. Hence the optimum time for maximum efficiency was found to be 12 h for both 1 M HCl and 0.5 M H_2SO_4.

As the time of immersion increases, process of adsorption of phytochemical constituents of CAF on metal surface takes place gradually upto the optimum immersion period after which desorption of CAF extract from mild steel surface results in reduction of inhibition efficiency.

Effect of temperature

The study was carried out carried out using NSW India Thermostat at different temperatures ranging from 303 K to 343 K for 1 h and the results are provided in tables 3 & 4. In HCl, the temperature studies reveal that at higher temperatures also the inhibition efficiency increased with increase in concentration of the inhibitor. The efficiency of the inhibitor was found to be 97.29% for 2.5 %v/v of CAF extract at 333 K. Further rise in temperature decreased IE.

In presence of CAF extract in 0.5 M H_2SO_4 the corrosion rate of mild steel increased with increase in temperature upto 323 K. The Inhibition efficiency was found to be maximum (94.52 %) at 323 K for 2.5 % v/v of the extract. Beyond 323K, the increase in temperature decreased the protective action for all concentrations of the inhibitor.

Table 3: Inhibition efficiencies at various temperatures studied for mild steel in 1 M HCl containing different concentrations of CAF

S. No	Conc(%) v/v	IE %				
		303 K	313 K	323 K	333 K	343 K
1	0.01	67.65	42.98	60.89	58.33	32.58
2	0.5	91.49	87.02	93.46	92.80	89.80
3	1	92.26	89.83	95.19	94.90	94.16
4	1.5	93.60	90.99	96.11	96.04	95.13
5	2	94.26	91.86	96.17	97.04	95.94
6	2.5	94.97	90.60	97.05	97.29	96.54

Table 4: Inhibition efficiencies at various temperatures studied for mild steel in 0.5 M H_2SO_4 containing different concentrations of CAF

S. No	Conc. (%) v/v	IE %				
		303 K	313 K	323 K	333 K	343 K
1	0.01	55.89	53.06	50.04	34.95	33.49
2	0.5	82.37	83.87	92.46	91.46	87.17
3	1	85.19	87.41	92.41	92.58	90.46
4	1.5	87.07	86.71	93.55	93.69	91.50
5	2	87.76	85.83	94.15	93.98	92.46
6	2.5	85.42	88.80	94.52	94.52	93.05

THERMODYNAMIC PARAMETERS

Thermodynamic parameters like free energy change ΔG, enthalpy ΔH, entropy ΔS were calculated to identify the type of adsorption and are given in Tables 5 & 6.

To obtain the standard adsorption free energy ($-\Delta G_{ads}$), ΔH_{ads} and ΔS, the following equations were used

$$k = (1/55.5) \exp [-\Delta G_{ads}/(RT)]$$

$$\ln k = (-\Delta H_{ads})/RT + \text{constant}$$

$$\Delta G = \Delta H - T\Delta S$$

Table 5: Thermodynamic parameters for the adsorption of inhibitor on mild steel in 1 M HCl

S. No	Conc % v/v	$-\Delta G_{ads}$ (kJ/mole)					ΔH_{ads} (kJ/mole)	$-\Delta S_{ads}$ (J/K/mole)
		303 K	313 K	323 K	333 K	343 K		
1	Blank	10.09	10.42	10.76	11.09	11.43	−9.866	0.0032
2	0.01	23.55	21.61	24.31	24.77	22.48	−20.255	0.0096

3	0.5	17.82	17.18	19.76	20.09	19.60	2.008	0.0647
4	1	16.31	16.09	18.77	19.18	19.35	11.679	0.0917
5	1.5	15.83	15.39	18.28	18.95	18.74	12.859	0.0938
6	2	15.39	14.93	17.55	18.83	18.47	15.459	0.1006
7	2.5	12.57	13.94	17.68	18.47	18.30	35.456	0.1599

Table 6: Thermodynamic parameters for the adsorption of inhibitor on mild steel in 0.5 M H_2SO_4

S. No	Conc % v/v	$-\Delta G_{ads}$ (kJ/mole)					ΔH_{ads} (kJ/mole)	$-\Delta S_{ads}$ (J/K/mole)
		303 K	313 K	323 K	333 K	343 K		
1	Blank	3.18	2.301	0.183	1.11	2.23	– 10.92	28.09
2	0.01	23.23	23.56	24.61	25.67	26.73	9.55	105.7
3	0.5	16.67	16.96	17.93	18.89	19.86	13.27	96.59
4	1	14.68	14.98	15.99	17.01	18.03	16.81	105.7
5	1.5	14.28	14.61	15.71	16.81	17.91	19.78	109.86
6	2	13.77	14.10	15.18	16.26	17.35	19.83	108.86
7	2.5	13.30	13.64	14.79	15.99	17.08	22.17	114.39

ADSORPTION ISOTHERM

The mechanism of corrosion inhibition may be explained on the basis of adsorption behaviour. The electrochemical process on the metal surface is likely to be closely related to the adsorption of the inhibitor and the adsorption is known to depend on the chemical structure of the inhibitor.

The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated from weight loss data. Data were tested graphically by fitting to various isotherms. A straight line was obtained on plotting log (θ/1 – θ) versus log C (figures 1 & 2) suggesting that the adsorption of the compounds from the medium on the mild steel surface follows Langmuir's adsorption isotherm.

The applicability of Temkin's adsorption isotherm (figures 3 & 4) verifies the assumption of mono-layer adsorption on a uniform, homogenous metal surface with an interaction in the adsorption layer.

Table 7: 1/Y values from the Langmuir isotherm for 1M HCl and 0.5M H_2SO_4

1/Y	303 K	313 K	323 K	333 K	343 K
HCl	2.6026	2.2058	1.8076	1.6910	1.3454
H_2SO_4	3.1833	3.0862	2.0550	1.7236	1.6082

The slope of log θ/1 – θ Vs log C gives the value of Y. From *Y*, 1/*Y* was calculated and is given in table 7. 1/*Y* gives the number of inhibitor molecules occupying one active site or the number of water molecules replaced by one molecule of the inhibitor. From the 1/*Y* values it is seen that more than one inhibitor molecule occupies one active site which proves its efficiency in both the media.

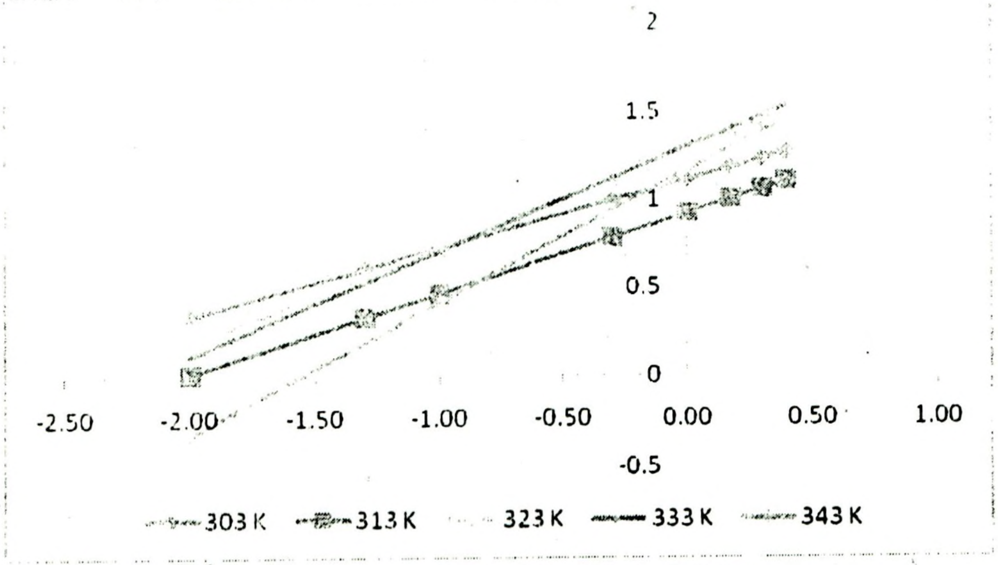

Fig. 2. Langmuir Isotherm for CAF in 1M HCl

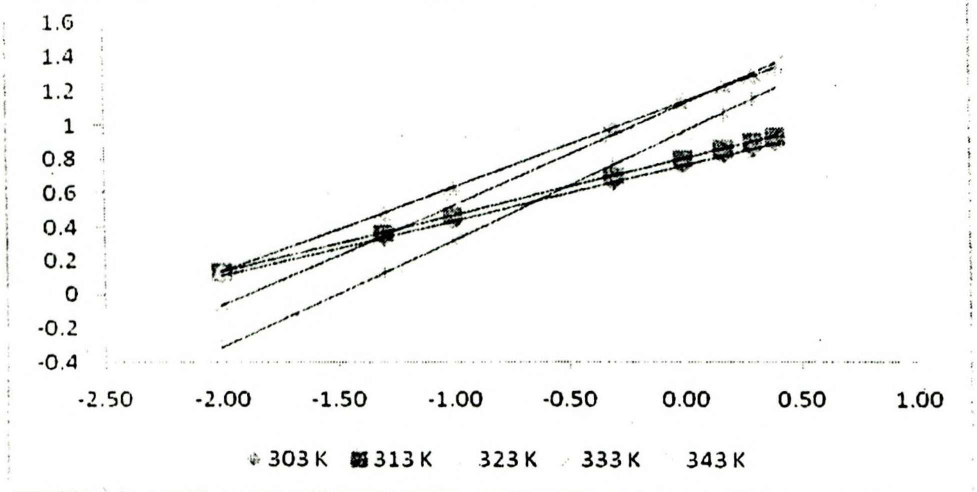

Fig. 3: Langmuir Isotherm for CAF in 0.5M H_2SO_4

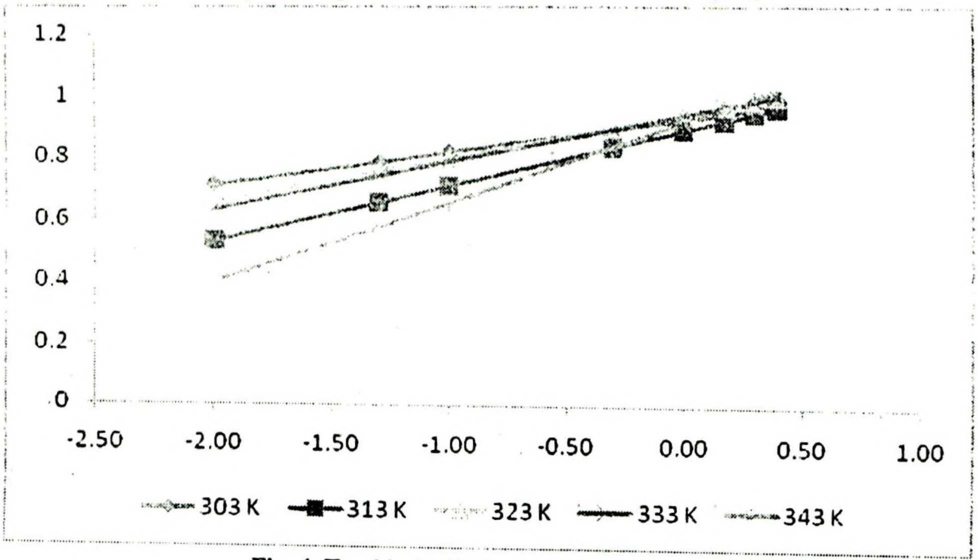

Fig. 4. Temkin Isotherm for CAF in 1M HCl

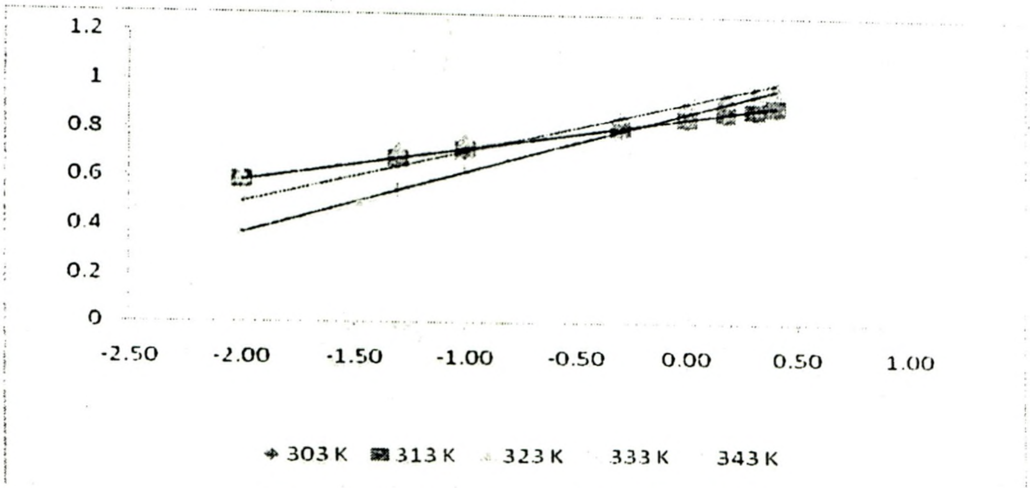

Fig. 5. Temkin Isotherm for CAF in 0.5M H_2SO_4

MECHANISM OF INHIBITION

A review of the phytochemical analysis of CA revealed the presence of the following constituents, 2,3,5-Trimethylphenol, 2-Ethylphenol, 2-Methoxy 4-ethyl phenol, 2,4-Methylene phenol, Dicaffeoyl-quinic acid, 4-Ethylphenol, 4-Methoxy 4-vinylphenol, Acetaldehyde, Caffeine, Caffeol, Caffeoyl-3-quinic acid, Caffetannic acid, Chlorogenic acid, Citric acid, Daturic acid, Guaiacol, Hypoxanthine, Isochlorogenic acid, Putrescine, Scopoletin, Spermidine, Spermine, Sugars, Tannic acid, Tannin, Theobromine, Theophylline, Trigonelline, Thiamine, Xanthine. (www.coffeescience.org)

In acidic solution, the constituents of the extracts may exist as protonated species and these protonated species adsorb on the cathodic sites of the mild steel and decrease the evolution of hydrogen.

The adsorption on the anodic sites through π electrons of aromatic ring and the lone pairs of nitrogen or oxygen atoms causes decrease in the anodic dissolution of the metal (since caffeine, caffetannic acid and chlorogenic acid are the main constituents in the seed coating of *Coffea arabica*).

CONCLUSION

The corrosion inhibition of mild steel in 1M HCl and 0.5 M H_2SO_4 offered by CAF extracts has been studied. Corrosion inhibitive action was examined by direct weight loss method. This method confirmed the effectiveness of the inhibitors. The main conclusion drawn from all the studies using acid extracts of CAF are :

The inhibitor efficiency of all acid extracts increased with increase in inhibitor concentration up to 2.5% (v/v) maximum efficiency being provided by 1 M HCl.

The protective action of the acid extracts increased with increase in the period of immersion upto 12 h in both 1M HCl and 0.5 M H_2SO_4 and after that, a decrease in inhibitor efficiency was observed. The inhibitor proved to be effective in 1 M HCl compared to 0.5 M H_2SO_4.