

Cassia auriculata extract as Corrosion inhibitor for Mild Steel in Acid medium

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Abstract: The inhibition efficiency of acid extract of flowers of Cassia Auriculata (CAF) plant on the corrosion of mild steel in 1 M HCl was investigated by weight loss measurements and electrochemical studies. The corrosion rate of mild steel and the inhibition efficiencies of the extract were calculated. The results obtained showed that the extract could serve as an effective inhibitor for the corrosion of mild steel in HCl media. Inhibition was found to increase with increasing concentration of the plant extract. The inhibitive action of plant extract is discussed on the basis of adsorption of stable complex at the mild steel surface. Theoretical fitting of different isotherms, Langmuir, Temkin, Freundlich and the thermodynamic model, were tested to clarify the nature of adsorption. Potentiodynamic Polarisation curves revealed that this inhibitor act as a mixed type inhibitor and the inhibition efficiency of up to 74.7% can be obtained.

Keywords: Cassia auriculata Flower (CAF), Mild steel, Temkin's adsorption isotherm, Potentiodynamic polarization.

INTRODUCTION

Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting MS from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in

different media^[1-16]. Plant extracts constitute several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant^[17-21] and its location^[22]. The extracts from the leaves, seeds, heartwood, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media^[20, 21, 23-34]. A summary of plants extracts used as corrosion inhibitors have recently been given in Okafor *et al.*^[21] and Raja and Sethuraman^[35]. The aim of the present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel. The

use of natural product will establish, simultaneously, the economic and environmental goals.

EXPERIMENTAL

1. SAMPLE PREPARATION

Rectangular samples of area 4x1 cm² have been cut from a large sheet of mild steel. The samples were polished, drilled a hole at one end and numbered by punching. During the study the samples were polished with 400 grade emery papers, degreased in a solution of non-toxic detergent, washed with distilled water, dried, weighed and stored in desiccators for further use.

2. EXTRACTION OF PLANT MATERIALS

The flowers were collected, shade dried and powdered. Plant materials are dried in shade so as to enrich the active principles in them, by reducing their moisture content. The extract was prepared by refluxing 25 g of powdered dry leaves and seeds in 500 mL of 1 M HCl for 3 h and kept overnight. Then it was filtered and the volume of the filtrate was made up to 500 mL using the same acid and this was taken as stock solution.

3. WEIGHT LOSS MEASUREMENTS

Polished specimens were initially weighed in an electronic balance. Weighed samples are immersed in 100 mL of the acid (1 M HCl) without and with different concentrations of the inhibitor for various intervals of time. They are then taken out and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed. The parameters used for the present study are given below

1. Time : 3 h, 6 h, 9 h, 24 h

2. Concentration of the inhibitor : 0.03%, 0.06%, 0.09%, 0.12%, 0.15, 0.18%(v/v)

3. Temperatures : (303 K , 313 K , 323 K , 333 K) ±2 K

From the change in weight of specimens the corrosion rate was calculated using the following relationship ,

$$\text{Corrosion rate} = \frac{82.75 \times W}{A \times T \times D}$$

W = Loss in weight in mg

A = surface area of the specimen (cm²)

T = Time in hrs

D = Density (7.2g/cm³)

4. POTENTIODYNAMIC

POLARISATION MEASUREMENT

Potentiodynamic polarisation studies were carried out using VSP primeton.100 ml of 1M HCl

without and with 0.15%(v/v) concentrations of the inhibitor was taken in an electrochemical cell. The polished electrode was then introduced. The electrode was placed at 0.8 mV to its open circuit potential. Thus the potential was scanned at 10 mV/sec towards the anodic direction in Tafel extrapolation. Applied potential vs. current was plotted and on extrapolation of linear portion to the corrosion potential gives the corrosion current. In anodic and cathodic plot, the slope of the linear portion gives Tafel constants 'b_a' and 'b_c' respectively. According to the Stern-Geary equation, the steps of the linear polarization plot are substituted to get corrosion current.

$$I_{\text{corr}} = \frac{b_a \times b_c}{2.303(b_a + b_c)R_p}$$

Where, R_p is polarization resistance.

Determination of inhibition efficiency

By Tafel method

$$I_{\text{corr}} = \frac{I_{\text{corr}} - I_{\text{corr}(1)}}{I_{\text{corr}}} \times 100$$

where,

I_{corr} is corrosion current without inhibitor

I_{corr(1)} is corrosion current with inhibitor.

5. IMPEDANCE STUDIES

Impedance measurements were carried out at various corrosion potentials. An ac sine wave of 10 mV amplitude was applied to the electrode. The frequency which is varied from 10 KHz to 100 MHz was superimposed at the open circuit potential. The results are presented in the form of Nyquist plot. All the measurements were presented in the corrosion potential. In Impedance method, the charge transfer resistance (R_{ct}) is obtained from the plots of Z' vs. Z'' (real part Vs imaginary part; Nyquist plot). The value (R_p+ R_s) corresponds to the point where the plot cuts Z axis to the point where the semicircle cuts the Z axis at high frequency. The difference gives the R_p values, which were substituted in the Stern-Geary equation to get

$$I_{\text{corr}} = \frac{b_a \times b_c}{2.303(b_a + b_c)R_{ct}}$$

The b_a and b_c values were experimentally obtained.

Table -I: Influence of concentration of inhibitor on percentage inhibition and corrosion rate.

S.No.	Inhibitor Concentration(v/v%)	Weight Loss(mg)	Corrosion Rate(mpy)	Percentage Inhibition Efficiency
1	Blank	11.5	4.06	-
2	0.03	6.90	2.43	40.0
3	0.06	6.10	2.15	46.9
4	0.09	5.70	2.01	50.0
5	0.12	3.00	1.05	73.9
6	0.15	2.90	1.02	74.7
7	0.18	5.60	1.97	51.0

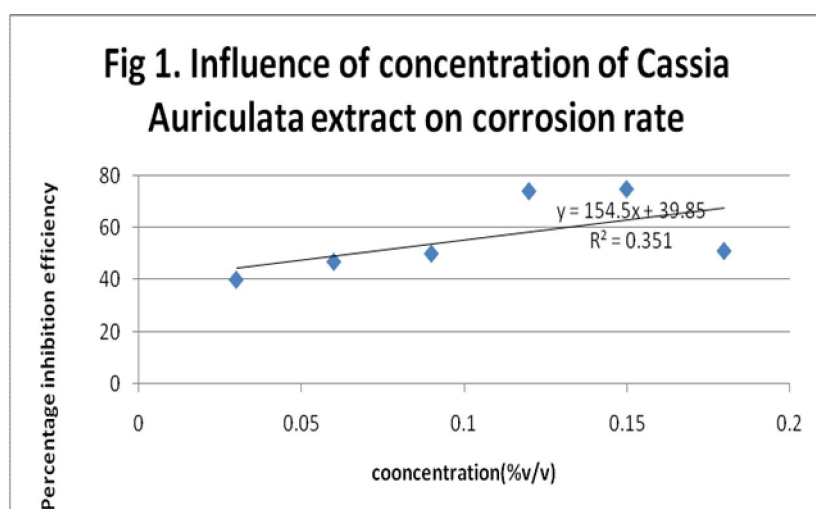


Fig: 1 Influence of concentration of Cassia auriculata flower extract on percentage inhibition efficiency.

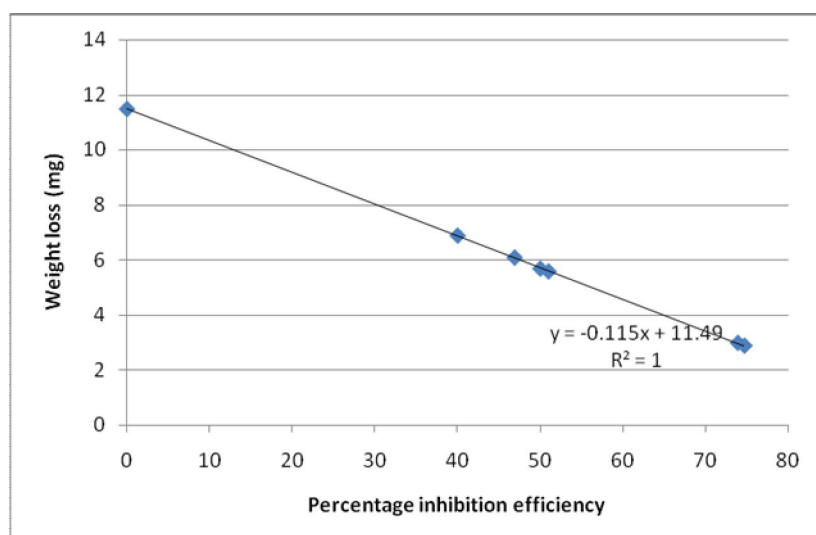


Fig: 2 correlation of weight loss and inhibition efficiency

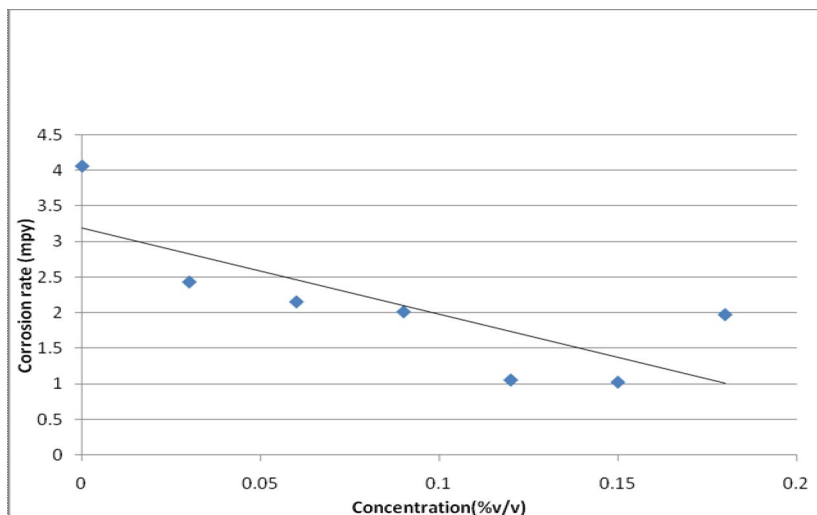


Fig: 3 Influence of concentration of cassia auriculata flower extract on corrosion rate

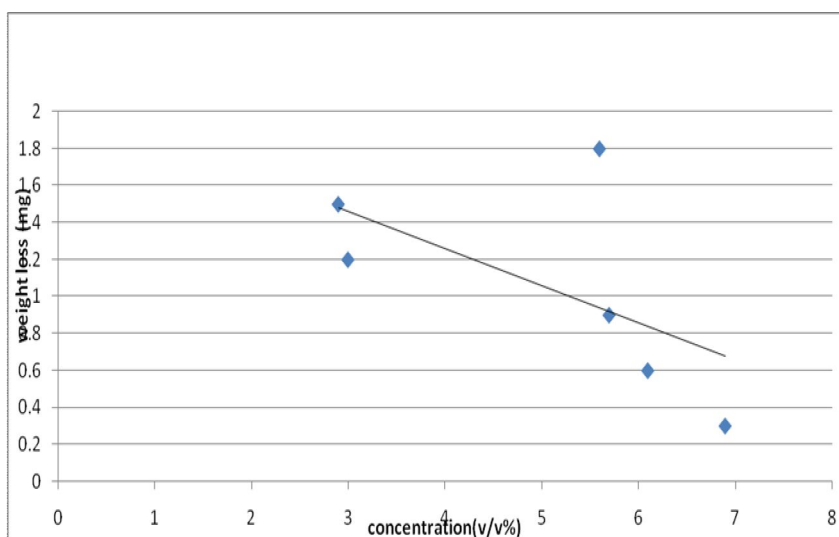


Fig: 4 Influence of concentration of inhibitor on weight loss

RESULTS AND DISCUSSION

MASS LOSS STUDIES

The inhibitor was tested for six different concentrations and their corresponding weight loss data are presented in **Table 1**. (**Figures 1-4**) The addition of inhibitors increases the IE, irrespective of the time of immersion. This may be due to the adsorption of phytochemical constituents of the extracts on the metal surface. The IE is 74.7 % at a concentration of 0.15% v/v. The results concerned with the effect of period of immersion at various concentrations of the inhibitors on mild steel in 1 M HCl are also shown in Table 2. The IE increases from 3 h to 6 h period of immersion and decreases from 9h to 24 h period of immersion. The decrease in IE with time may be attributed to various factors such as an increase in the ferrous ion concentration.

EFFECT OF TEMPERATURE

The effect of temperature on the inhibitory action of the inhibitor was determined by mass loss method at 0.15%(v/v) concentration at different temperatures (303, 313, 323, and 333) ± 2 K for a fixed immersion time of 3hrs. The tabulated data (**Table 3**) reveal that, at a concentration of 0.15%v/v of the inhibitor the corrosion rate has increased with rise in temperatures. Though the C.R has increased with temperature for a given concentration of the inhibitor, there is no regular trend in the change of inhibition efficiency. This may be explained on the basis of the time lag between the process of adsorption and desorption. However, the inhibitor could be effectively used at 313K and maximum efficiency being 81.78%.

Table - II: Inhibition efficiency of mild steel in 1MHCl in the presence of Cassia Auriculata Flower extract at 303K at different time period

S.No.	Immersion period	Inhibitor concentration(v/v%)	Corrosion rate(mpy)	Percentage Inhibition efficiency
1	3 hours	Blank	10.2	-
		0.15	1.02	74.7
2	6 hours	Blank	6.49	-
		0.15	0.582	86
3	9 hours	Blank	21.234	-
		0.15	1.829	69
4	24 hours	Blank	28.85	-
		0.15	2.95	31

Table - III: Protection Performance of Cassia Auriculata Flower extract on mild steel in 1MHCl for 3 hrs at different temperatures

S. No.	Temperature (K)	Inhibitor Concentration (v/v%)	Corrosion Rate (mpy)	Percentage Inhibition Efficiency	Log C.R/T	1/T x 10 ³
1	303	Blank	10.2	-	-1.87	3.30
		0.15	1.02	74.7	-2.4	
2	313	Blank	0.46	-	-2.83	3.19
		0.15	0.10	81.78	-3.49	
3	323	Blank	8.29	-	-1.59	3.09
		0.15	1.72	60.29	-2.27	
4	333	Blank	17.02	-	-1.29	3.00
		0.15	9.48	42.9	-1.56	

INTERPRETATION OF THERMODYNAMIC DATA

Activation energy (E_a) and thermodynamic data, such as change in free energy (ΔG_{ads}), enthalpy (ΔH), and entropy (ΔS) for mild steel in 1M HCL in the presence and in the absence of the inhibitor was calculated are listed in the table 4. The activation energy at different temperatures and 0.15%(v/v) concentration of the inhibitor in HCL is calculated by plotting log C.R vs. 1/T (**figure 5 and 6**). E_a values for inhibited systems are lower than those for uninhibited system indicating that all the inhibitors exhibit high I.E at elevated temperatures. The range of E_a is 68.2-32 kJ/mol for CAE in 1N HCL. The negative values of ΔG_{ads} (-11.73 to -12.89kJ) suggest the strong interaction of the inhibitors molecules whereas low value of ΔG_{ads} indicated spontaneous adsorption of inhibitors on MS surface. The negative values of ΔH (58.9-29.48 kJ/mol) indicate that the adsorption of inhibitor molecules is an exothermic reaction. The change in entropy was found to be greater than zero 0.136. This indicates that the reaction is irreversible. It

is clear that, the complete desorption of the inhibitor is not possible.

Applicability of adsorption isotherms

The surface coverage (θ) values for different concentrations of the inhibitors in the both medium have been evaluated from the weight loss data. At any instant a fraction θ of the metal surface is covered by the inhibitor molecules and the uncovered fraction ($1 - \theta$) reacts with acid as it does in the absence of the inhibitor.

The nature of the inhibitor interaction with the corroding surface has been deduced from the adsorption characteristics of the inhibitor. Surface coverage θ values are much useful to measure the adsorption characteristics. The surface coverage of an inhibitor at any concentration is calculated using the equation,

$$\theta = \frac{W_0 - W}{W_0}$$

Where W_0 and W are the weight loss without and with inhibitor respectively and the values at different concentrations are presented in table 5.

The data were tested graphically to find a suitable adsorption isotherm. A plot of $\log [\theta / (1 - \theta)]$ against $\log C$ (figure 7) shows a straight line ($R > 0.9$) indicating that adsorption follows the Langmuir adsorption isotherm. It is observed that although these plots are linear, the gradients are never unity, contrary to what is expected for ideal Langmuir adsorption isotherm equation. Plant extract contains organic compounds having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slopes values from unity. The number of active sites of the surface occupied by one molecule of the inhibitor is given by the value of $(1/y)$. A straight line was obtained when the surface coverage was plotted against $\log C$ for the inhibitor. This shows that the adsorption obeys a Temkin adsorption isotherm, which is graphically represented in figure 8. The plots of $\log \theta$ vs $\log C$ are shown in figure 9. The linearity shows that the adsorption of the inhibitor on mild steel surface follows Freundlich isotherm.

Potentiodynamic polarization results

The various electrochemical parameters calculated from Tafel plot (figures 10) are given in

Table 6. The lower corrosion current density (I_{corr}) values in the presence of inhibitor without causing significant changes in corrosion potential (E_{corr}) (-429.261 to -435.856 mv) suggests that the compound is mixed type inhibitor (i.e., inhibit both anodic and cathodic reactions) and are adsorbed on the surface thereby blocking the corrosion reaction. Since b_a is greater than b_c suggesting that though the inhibition is under mixed control, the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.

- (a) Tafel plot for mild steel in 1M HCl.
- (b) Tafel plot for mild steel in 1MHCl with CAF.

Electrochemical impedance spectroscopy results

Impedance diagram (Nyquist plot) obtained for mild steel 1N HCl in the presence of various concentrations of the inhibitor is depicted in figure 11. They are perfect semicircles and this was attributed to charge transfer reaction. Impedance parameters derived from Nyquist plots are tabulated in Table 7. It can be seen that the resistance has increased and C_{dl} values has decreased. Decrease in C_{dl} , which can result from an increase in thickness of electrical double layer, suggests that the inhibitor molecules function by adsorption at the metal-solution interface.

Table - IV: Thermodynamic parameters for mild steel corrosion in 1MHCl with Cassia Auriculata flower extract

S.No.	E_a (kJ/Mol)	$-\Delta G_{ads}$ (kJ/Mol)				ΔH (kJ/Mol)	ΔS (kJ/Mol/K)
		303K	313K	323K	333K		
Blank	68.2	-	-	-	-	58.5	-
0.15	32.0	11.73	12.12	12.51	12.89	29.48	0.136

Table - V: Influence of concentration of CAF on surface coverage.

S.No.	Inhibitor concentration(v/v%)	Log C	θ	Log θ	Log($\theta/1-\theta$)	Log(θ/C)	Log(1- θ)
1	Blank	-	-	-	-	-	-
2	0.03	-1.5229	0.40	-0.39	-0.18	1.1249	-0.22
3	0.06	-1.2218	0.47	-0.32	-0.05	0.8939	-0.28
4	0.09	-1.0458	0.50	-0.30	0.00	0.7447	-0.30
5	0.12	-0.9208	0.74	-0.13	0.45	0.7900	-0.59
6	0.15	-0.8239	0.75	-0.12	0.47	0.6990	-0.60
7	0.18	-0.7447	0.51	-0.29	0.02	0.4523	-0.31

Table - VI: The corrosion parameters for mild steel in 1MHCl with CAF extract from polarization studies

S.No.	Environment	E_{corr} Vs SCE (mv)	B_c (mv)	B_a (mv)	I_{corr} (μA)
1	Blank	-429.261	154.1	332.2	1411.38
2	0.15	-435.856	144.4	273.6	1037.52

Table - VII: The corrosion parameters for mild steel in 1MHCl with CAF extract from impedance studies

S.No.	Environment	R_t (ohm)	Cdl(F)
1	Blank	49.59	0.1597
2	0.15	65.66	0.0803

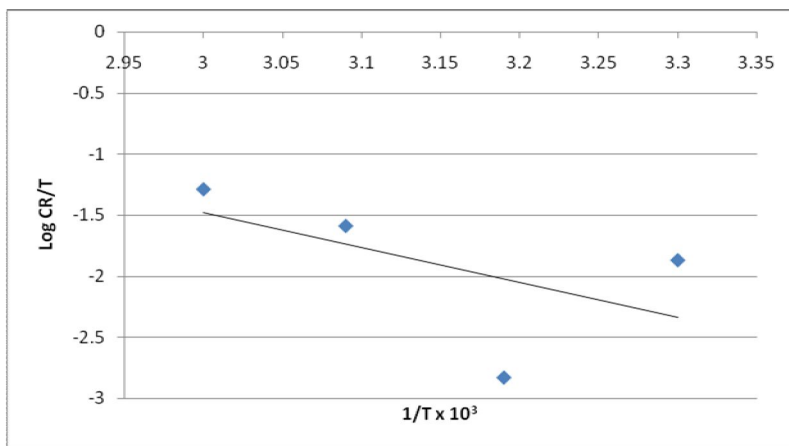


Fig: 5 Arrhenius Plot for 1MHCl

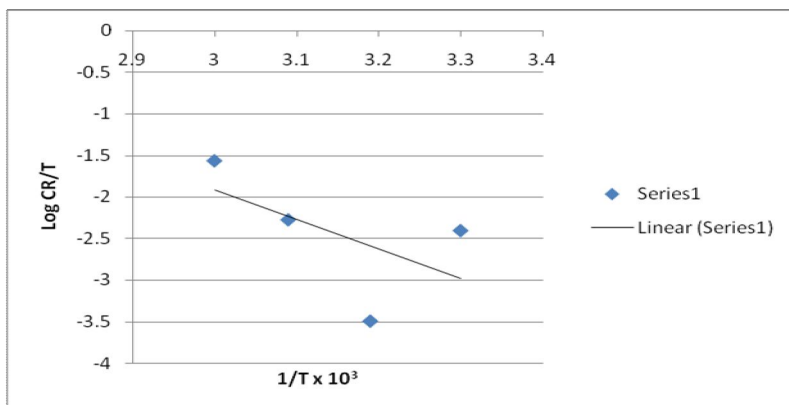


Fig: 6 Arrhenius Plot for CAF

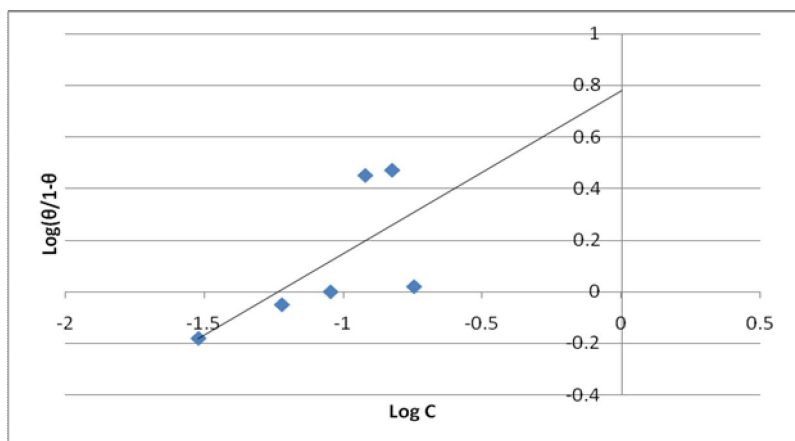


Fig: 7 Langmuir adsorption isotherm for the inhibition of corrosion of mild Steel by CAF in acid medium

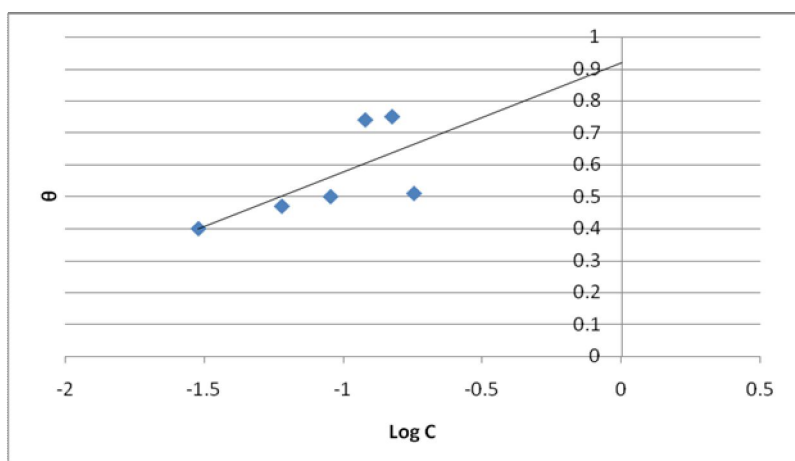


Fig: 8 Temkin adsorption isotherm for the corrosion inhibition of mild steel by CAF in acid medium

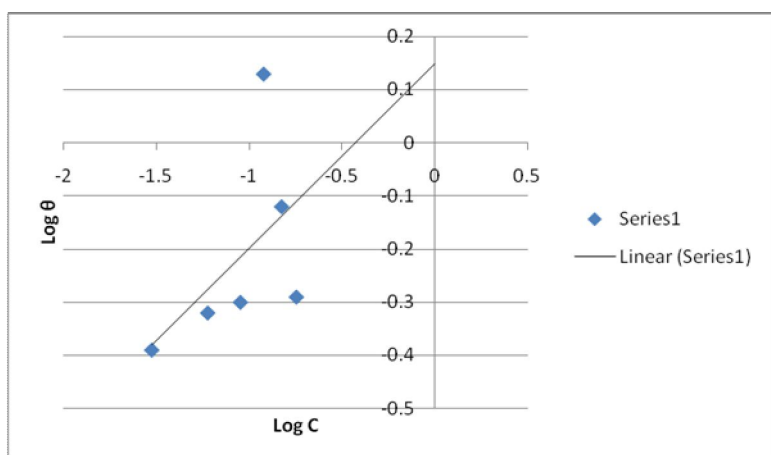


Fig: 9 Freundlich adsorption isotherm for the corrosion inhibition of mild Steel by CAF in acid medium

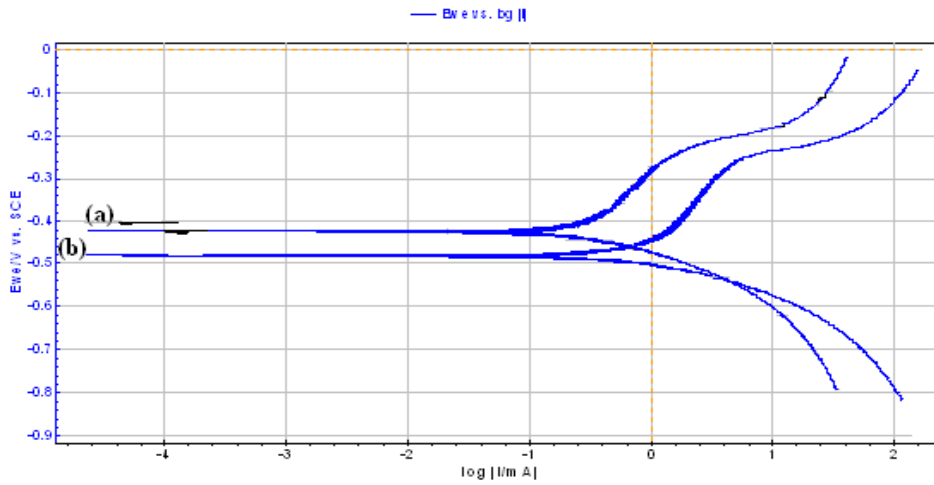


Fig: 10 Tafel Plot

- (a) Potentiodynamic polarisation of corrosion of Mild Steel in 1M HCl
- (b) Potentiodynamic polarisation of corrosion of Mild Steel in the presence of CAF

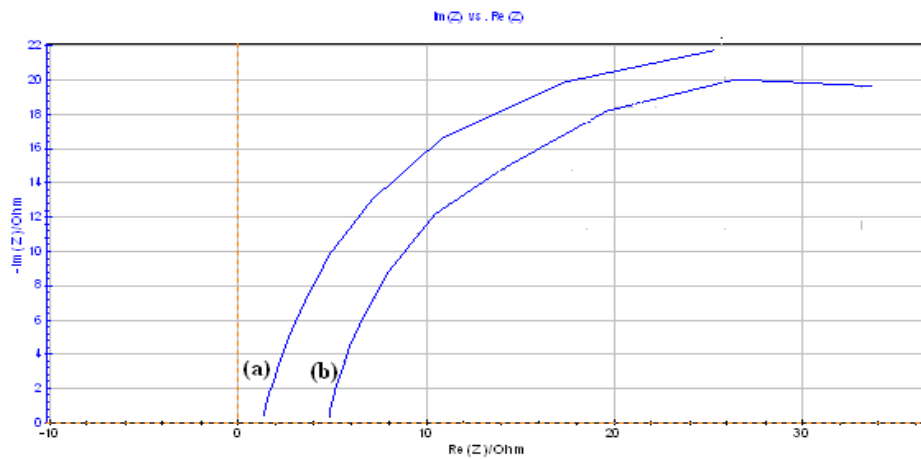


Fig: 11 AC impedance of mild steel immersed in various environments

- (a) Nyquist diagram for mild steel in 1MHCl
- (b) Nyquist diagram for mild steel in the presence of CAF

CONCLUSION

The following conclusions were made from the following studies,

1. The corrosion rate of mild steel in 1MHCl decreases with increase in concentration of CAF.
2. The inhibition efficiency increases with respect to the concentration of the inhibitor and decreases with rise in temperature from 303K to 333K.
3. The maximum inhibition efficiency of CAF is found to be 74.7% at 0.15(%v/v) of inhibitor from mass loss studies at 303K.
4. The decrease in the energy of activation values indicates that the addition of plant extract metal dissolution and also indicates that decrease in the adsorption of the inhibitor on mild steel surface with increase in temperature.
5. The negative values of ΔG indicates that the CAF is chemically adsorbed and spontaneous adsorption of inhibitors on the surface of mild steel.

6. The higher value of heat of adsorption also showed that the inhibition efficiency decreased with rise in temperature.
7. The low positive enthalpy value of adsorption is evident that the CAF was strongly adsorbed on the mild steel was probably physisorption.
8. The adsorption of CAF on mild steel surface from the acid solution followed Tempkin, Langmuir and Freundlich adsorption isotherms.
9. The results of polarization study showed that the formulation function as a mixed type inhibitor, more predominantly controls the anodic reactions.
10. The AC impedance spectral studies revealed the formation of a film with higher resistance than that of the blank solution.

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