Studies on Corrosion Inhibition of *Musa acuminata* Flower Extract on Mild Steel in Acid Medium

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The inhibition effect of acid extract of *Musa acuminata* flower (MAF) on the corrosion of mild steel in 1 N hydrochloric acid solution has been investigated by potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss methods. The corrosion inhibition efficiency increases with increasing flower extract concentration. Cathodic and anodic polarization curves showed that the *Musa acuminata* flower is a mixed type inhibitor. The effect of temperature on the corrosion behaviour of mild steel in 1 N HCl in the absence and presence of flower extract was studied in the temperature range of 30-80 ºC. Thermodynamic consideration reveals that the adsorption of *Musa acuminata* flower extract on mild steel surface is spontaneous and followed Langmuir and Temkin adsorption isotherms. The weight loss measurement results were close to electrochemical studies. A possible mechanism for the inhibition behaviour of flower extract by physical adsorption of its phytochemical components on the surface of the metal has been proposed.

Key Words: *Musa acuminata*, Corrosion inhibitor, Mild steel, Polarization, EIS, Weight loss, Adsorption isotherm.

INTRODUCTION

Corrosion is a major degradation process by which the components and structures in industry and infrastructure fail prematurely and causes significant economic losses. Corrosion of assets and protection of the environment are very important issues which affect the country. Corrosion occurs in metals in the presence of moisture, oxygen and pollutants[1,2]. Mild steel is widely used in many industries due to its excellent mechanical properties, easy availability and fabrication and low cost[3,4].

One of the best methods to protect metals against corrosion is by using inhibitors. Inhibitors are known for their specificity of action[5]. Most of the inhibitors used are synthesized from compounds having heteroatom and are toxic to the environment. This led to the search of green corrosion inhibitors[6,7].

The extracts from the parts of plants like peels, seeds, fruits, shells, leaves contain organic compounds like amino acids, tannin and are known to have inhibitive action. A large number of natural products like *Musa sapientum* (peels)[6], *Solanum tuberosum* (leaves)[8], *Eclipta alba* (leaves)[9], Beet root (root)[10], *Vernonia amygdalina* (leaves)[11], Black pepper (seed)[12], *Euphorbia falcata* (aerial parts)[13], *Cocos nucifera* (petiole)[14], Aloe Vera (leaves)[15], *Mangifera indica* (bark and leaves)[16], Ginseng root[17], *Zenthoxylum alatum* (fruits)[18], *Azadirachta indica* (matured leaves, seeds and roots)[19], *Uncaria gambir*

(plant)[20], *Oxandra asbeckii* (leaves)[21], *Cola acuminate* and Nicotiana (nuts and leaves)[22] have been reported to be effective acid corrosion inhibitors for mild steel.

In present study the extract from flowers of *Musa acuminata* is used to study corrosion inhibition on mild steel in 1 N HCl by weight loss and polarization methods. Banana and plantains have played interesting and important roles in the history of human civilization. Banana is a monoecious plant of *Musa* species. The banana inflorescence has male flowers at the tip, several sterile flowers and female flowers behind. The banana flower is treated in cuisines as a vegetable. The cut ends of the banana flower leak a sap that will stain skin and other surfaces black. Banana flowers have nutritive benefits as they are a good source of vitamins A, B and C, potassium, magnesium, phosphorus, calcium and iron. It is used in the treatment of bronchitis, constipation and ulcers. It is good for diabetics, reduces painful excess menstrual bleeding, enhance milk supply in lactating mothers[23,24].

Studies by Azizah Mahmood *et al.*[25] show that banana flower *Musa paradisiaca* contains chemical constituents such as tannin, flavonoid, saponin, alkaloid and phenols. The present study aims to investigate the inhibitive properties of *Musa acuminata* flower (MAF) on mild steel corrosion using weight loss method and electrochemical measurements. The thermodynamics parameters are also reported here.

EXPERIMENTAL

Preparation of flower extract: Flowers of cultivar variety of *Musa acuminata* called Nendran were collected from the banana farm at Thirumalayampalayam, Coimbatore, India. The slim, nectar-rich, tubular toothed, white flowers were separated from the purple thick, waxy hood like bract and shadow dried. 5 % stock solution of the inhibitor material MAF extract was prepared by refluxing 12.5 g of dried banana flower powder with 250 mL of 1 N HCl for 3 h and filtering through filter paper. The residue was repeatedly washed with small amount of 1 N HCl and the filtrate was made up to 250 mL. The 5 % stock solution was used in preparing different concentrations of the extract from 0.05-2.0 % v/v[26]. The test solutions were prepared using of analytical grade hydrochloric acid and double distilled water.

Electrodes: The corrosion tests were performed on mild steel sample. Mild steel sheet of 2 mm thickness was mechanically cut into coupons of 5 cm × 1 cm size with a hole of uniform diameter at the upper end to facilitate suspension of the coupon in the test solution. The working surface was abraded with a series of emery papers (SiC) of 200, 400, 800 grade. The specimens were washed with doubly distilled water, degreased with acetone and dried. The treated coupons were stored in desiccator before use for corrosion studies to prevent contamination.

For electrochemical studies, a mild steel rod of 15 cm long and 5 mm diameter covered by Teflon leaving 0.19625 cm^2 of surface area was exposed to the solution[27].

Weight loss measurements: Preweighed mild steel specimens were immersed in a beaker containing 100 mL of 1 N HCl with different concentration of flower extract ranging from 0.05, 0.10, 0.50, 1.00, 1.50, 2.00 v/v % using glass hooks for 1, 3, 5 and 7 h at 30 ºC. After the specified time the coupons were removed from test solutions, washed thoroughly with distilled water, dried and then weighed. The difference in weight was taken as weight loss in milligrams. All the experiments were performed in triplicate and average values are reported[28].

The corrosion rate (CR) was calculated by the following equation:

$$\text{Corrosion rate (mpy)} = \frac{534W}{DAT} \quad (1)$$

where mpy is mils per year, W is weight loss of specimen in milligrams, D is density of the specimen in g/cm^3, A is the area in square inches and T is the time of exposure of specimen in hours.

From the corrosion rate (CR), the surface coverage (θ) and inhibition efficiency (IE %) were calculated using:

$$\theta = \frac{C_R^\circ - C_R^i}{C_R^\circ} \quad (2)$$

$$\text{Inhibition efficiency (\%)} = \theta \times 100 \quad (3)$$

where θ is the surface coverage, C_R° and C_R^i are the corrosion rate in the absence and presence of inhibitor, respectively.

Potentiodynamic polarization studies: Potentiodynamic polarization was carried out for mild steel in the absence and presence of inhibitor. A frequency response analyzer PARASTAT 2273 and IBM personal computer which automatically controls linear polarization and Tafel polarization were used for the polarization study. The data was analyzed using computer software. Polarization measurements were performed to evaluate the corrosion kinetics parameters, such as I_{corr}, Tafel slopes b_a and b_c[28].

Electrode surface preparation: The mild steel rod coated with Teflon exposing an area of 0.19625 cm^2 was polished using 120, 200, 400, 600, 1000 and 1200 emery papers, degreased using acetone and then placed in test solution for 10 min before taking the measurement.

Polarization cell assembly: Experiments were carried out in three electrode polarization cells consisting of mild steel rod of 15 cm long and 5 mm in diameter embedded in specimen holder as working electrode (WE), a large area platinum mesh of negligible impedance as counter electrode (CE), a saturated calomel electrode as reference electrode (RE) and 100 mL of electrolyte. The temperature of the electrolyte was maintained at 30 ºC[28].

The polarization measurements were carried out from the potential range of -200 mV to +200 mV with respect to open circuit potential in absence and presence of inhibitor at a scan rate of 1 mV/s. The experiments were carried out in 1 N HCl with various concentrations of the inhibitor. The log of current and the corresponding potentials were fed into the plotter and potential E *versus* log I plot was obtained. The corrosion current I_{corr} was obtained from the Tafel plot by extrapolation of the linear portion of the curve to E_{corr}[29]. The slope of the linear region gives the Tafel slopes b_a and b_c which were calculated using "POWER SHOOT" software. The inhibitor efficiency was calculated using the expression:

$$\text{Inhibition efficiency (\%)} = \frac{I_{corr}(\text{Blank}) - I_{corr}(\text{Inh})}{I_{corr}(\text{Blank})} \quad (4)$$

where I_{corr} (Blank) and I_{corr}(Inh) are corrosion currents without and with inhibitor, respectively.

Electrochemical impedance measurements: The electrochemical impedance measurements were carried out for mild steel in acidic media using PARASTAT 2273-Advanced electrochemical system. The impedance measurement was made at corrosion potentials over a frequency range of 2-100 MHz with signal amplitude of 10 mV. The results are presented in the form of Nyquist plot. The real part (Z') and the imaginary part (Z") were measured at various frequencies and a plot of Z' *versus* Z" was made. From the plot, the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated using POWER SHOOT software. Impedance measurements were carried out for mild steel in 1 N HCl with and without inhibitor for selected concentration and the inhibitor efficiency (IE) was calculated using the equation[30]:

$$\text{IE (\%)} = \frac{R_{ct}(\text{Inh}) - R_{ct}(\text{Blank})}{R_{ct}(\text{Inh})} \quad (5)$$

where R_{ct} (Inh) and R_{ct} (Blank) are charge transfer resistances with and without inhibitor, respectively.

I_{corr} can be calculated from the Stern Geary equation:

$$I_{corr} = \frac{b_a \times b_c}{2.303(b_a + b_c)} \times \frac{1}{R_{ct}} \quad (6)$$

where b_a, b_c are the Tafel slopes and R_{ct} is the charge transfer resistance.

Thermodynamics parameters: Various thermodynamic parameters such as activation energy (E_a), free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) were calculated using the following equations.

The apparent activation energies (E_a) for the corrosion in absence and presence of inhibitor were evaluated from Arrhenius equation:

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{1/T_1 - 1/T_2}\right] \tag{7}$$

where K_1, K_2 are the corrosion rates at temperature T_1 and T_2 respectively.

The free energy of adsorption has been calculated from the equilibrium constant of adsorption using the expression:

$$K = \frac{1}{55}\exp\left[-\frac{G_{ads}}{RT}\right] \tag{8}$$

where 55 is the concentration of water in mol/L, $K = \theta/C(1-\theta)$ (from Langmuir equation), θ is degree of coverage on the metal surface, C is concentration of inhibitor[30].

$$\Delta G_{ads} = -RT \ln(55.5\,K)$$

Enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption can be calculated from the values of free energy of adsorption (ΔG_{ads}) using Gibbs-Helmholtz relationship:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \tag{9}$$

The slope and intercept of the line obtained by plotting ΔG_{ads} *versus* T furnished ΔS_{ads} and ΔH_{ads} respectively[27,31].

Scanning electron microscopy (SEM): The surface analysis of the samples were carried out using 'scanning electron microscopy'. The treated specimens were immersed 1 N HCl containing 2 % v/v concentration of flower extract for 5 h and the specimens were taken out gently, rinsed and dried without disturbing the surface.

RESULTS AND DISCUSSION

Weight loss, corrosion rate and inhibition efficiency: Weight loss measurements of mild steel subjected to the effect of 1 N HCl in the absence and presence of *Musa acuminata* flower (MAF) extract of various concentrations were made for 1, 3, 5 and 7 h of immersion at 30 ºC. The results obtained are presented in Table-1. Fig. 1 clearly shows a reduction in weight loss of the mild steel coupons in the presence of MAF extract compared to the blank. Inspection of the figure further reveals that loss in weight of the coupons decreases as the concentration of the inhibitor increases.

The calculated values of corrosion rate (mpy) for mild steel in 1 N HCl in the absence and presence of MAF extract of different concentrations are shown in Table-2. The result shows that the corrosion rate for mild steel is lower in the presence of the extract compared to the blank. The decrease in weight loss and corrosion rate of mild steel in the presence of the extract are the evidences that the extract of *Musa acuminata* flowers inhibit the corrosion of mild steel in acidic environment.

TABLE-1				
WEIGHT LOSS OF MILD STEEL IN ABSENCE AND PRESENCE OF MAF EXTRACT IN 1 N HCl AT VARIOUS IMMERSION PERIODS				
Concentration of extract (% v/v)	Weight loss (mg)			
	1 h	2 h	3 h	4 h
Blank	33.1	57.3	105.5	164.9
0.005	16.5	28.1	51.2	63.1
0.01	13.5	23.2	41.0	33.8
0.05	5.3	9.1	13.3	21.1
0.10	4.0	6.3	11.1	12.0
0.50	3.2	5.2	9.9	11.1
1.00	2.2	4.0	4.3	7.3
1.50	2.1	3.2	4.1	5.2
2.00	1.9	3.0	3.0	5.0
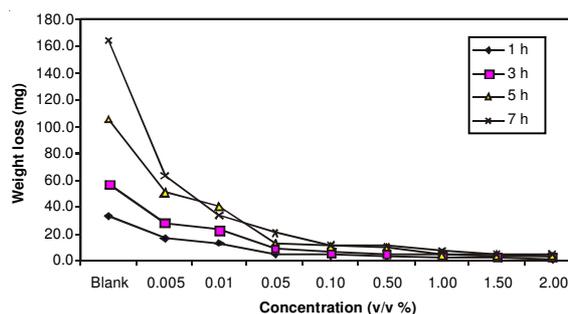
Fig. 1.　Variation of corrosion rate with different concentration of *Musa acuminata* extract at 303 K

TABLE-2				
VARIATION OF CORROSION RATE WITH EXPOSURE TIME FOR MILD STEEL IMMERSED IN 1 N HCl WITH VARIED CONCENTRATION OF MAF EXTRACT				
Concentration of extract (% v/v)	Corrosion rate (mpy)			
	1 h	3 h	5 h	7 h
Blank	1450.77	837.15	924.81	1032.51
0.005	723.20	410.54	448.82	395.10
0.010	591.71	338.95	359.41	211.64
0.050	232.30	132.95	116.59	132.12
0.100	175.32	92.04	97.30	75.14
0.500	140.26	75.97	86.78	69.50
1.000	96.43	58.44	37.69	45.71
1.500	92.04	46.75	35.94	32.56
2.000	83.28	43.83	26.30	31.31

Table-3 showed the calculated values of inhibition efficiency for MAF extract. The inhibition efficiency was observed to increase with increase in concentration of extract, probably due to an increase in the metal surface area covered by the nutrients in the extract.

TABLE-3				
PERCENTAGE INHIBITION EFFICIENCY OF MILD STEEL IN MAF EXTRACT IN 1 N HCl AT DIFFERENT CONCENTRATIONS AND DIFFERENT IMMERSION PERIODS				
Concentration of extract (% v/v)	Percentage inhibition efficiency			
	1 h	3 h	5 h	7 h
0.005	50.15	50.96	51.47	61.73
0.010	59.22	59.51	61.14	79.5
0.050	83.99	84.12	87.39	87.2
0.100	87.92	89.01	89.48	92.72
0.500	90.33	90.93	90.62	93.27
1.000	93.35	93.02	95.92	95.57
1.500	93.66	94.42	96.11	96.85
2.000	94.26	94.76	97.16	96.97

The inhibitive effect of MAF extract could be attributed to the presence of some phytochemical constituents in the flower. The phytochemical composition of the MAF extract is tannin, flavonoid, saponin, alkaloid and phenols. These compounds contain oxygen and nitrogen atoms which are the centres of adsorption. It could be assumed that the extracts establish their inhibitive action through adsorption of the phytochemical component molecules on the metal surface. This adsorption process creates a barrier between the metal and the corrosive medium leading to inhibition of corrosion. Consequently inhibition efficiency increases as metal surface is covered by the adsorbed molecules[32].

Electrochemical impedance spectroscopy (EIS): The corrosion behaviour of mild steel in 1 N HCl in the absence and presence of MAF extract was studied by EIS at 30 ºC. Nyquist plots of mild steel in uninhibited and inhibited acidic solutions containing various concentrations of MAF extract displayed semicircles as shown in Fig. 2. These plots indicate that the impedance response of mild steel changed with addition of MAF extract. Table-4 gives the impedance parameters derived from the Nyquist plots.
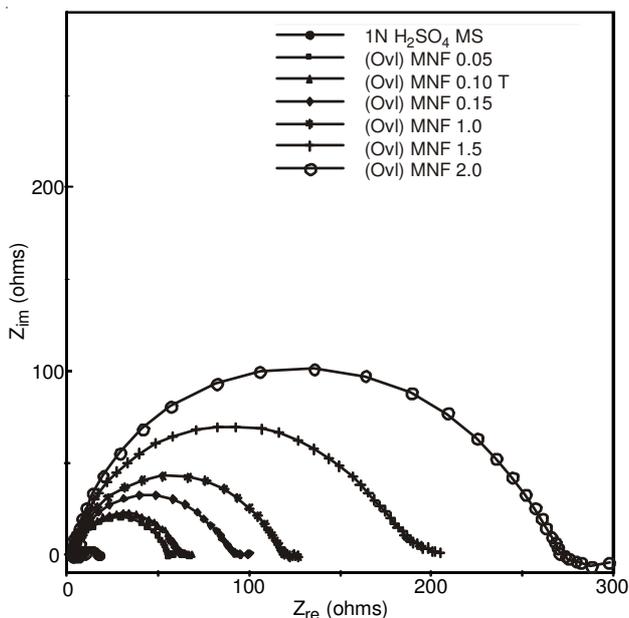
Fig. 2.   Nyquist plots showing effect of *Musa acuminata* flower extracts on corrosion of mild steel in HCl medium

TABLE-4
IMPEDANCE PARAMETERS FOR THE CORROSION OF MILD STEEL IN 1 N HCl IN THE ABSENCE AND PRESENCE OF DIFFERENT CONCENTRATIONS OF MAF EXTRACT AT 30 ºC

Concentration of extract (% v/v)	C_{dl} ($\mu F\ cm^{-2}$)	R_{ct} (ohm cm^2)	IE η_e (%)
Blank	1.986×10^{-4}	8.63	–
0.05	1.878×10^{-5}	46.64	81.50
0.10	1.096×10^{-5}	55.77	84.53
0.50	1.145×10^{-5}	82.09	89.49
1.00	1.184×10^{-5}	105.60	91.83
1.50	9.143×10^{-5}	173.50	95.03
2.00	9.954×10^{-5}	252.40	96.58

In EIS, the inhibition efficiency (η_e %) was calculated from charge transfer resistance using the equation:

$$\eta_e\ (\%) = \left\{ \frac{(R_{ct} - R_{ct}^{\circ})}{R_{ct}} \right\} \times 100 \qquad (10)$$

where R_{ct}° and R_{ct} are the charge transfer resistance values without and with the extract.

The inhibition efficiency [η_e (%)] and double layer capacitance C_{dl} values are shown in Table-4. The inhibition efficiency increased while the C_{dl} values decreased with increasing concentration of MAF extract. The decrease in C_{dl} values could be due to decrease in local dielectric constant and/or an increase in the thickness of the electric double layer. This suggests that the nutrients of the extract function through adsorption at the solution interface[33].

The EIS spectra were analyzed using the equivalent circuit (Fig. 3) which revealed a single charge transfer reaction. The diameter of the capacitance loop obtained in 1 N HCl solution increased in the presence of MAF extract indicating corrosion inhibition behaviour. The R_{ct} values increase with increase in the concentration of the inhibitor which is in accordance with the results obtained by weight loss method.
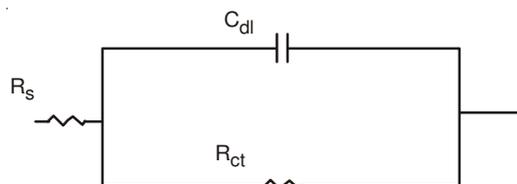
Fig. 3.   Electrical equivalent circuit for a.c. impedance measurement for mild steel in HCl

Potentiodynamic polarization: The polarization behaviour of mild steel in 1 N HCl in absence and presence of various concentrations (0.05, 0.10, 0.50, 1.00, 1.50, 2.00 % v/v) of inhibitor is shown in Fig. 4. Electrochemical parameters like corrosion potential (E_{corr}), corrosion current density (I_{corr}) and Tafel slopes (cathodic, b_c and anodic, b_a) were calculated from Tafel plots. The results of electrochemical parameters are represented in Table-5. The maximum decrease in I_{corr} was observed for the MAF extract at 2 % v/v. The E_{corr} values of the MAF extract shifted towards both cathodic and anodic directions. This indicates that, the both anodic and cathodic reactions of mild steel electrode were inhibited with increasing concentration of the flower extract. These results suggest that not only the addition of MAF extract reduces anodic dissolution but also retards the hydrogen evolution.

These results revealed the mixed type behaviour of the studied inhibitor.

Inhibition efficiency [η_e (%)] was obtained from the equation:

$$\eta_e(\%) = \left(\frac{I_{corr\,(blank)} - I_{corr(Inh)}}{I_{corr(blank)}} \right) \times 100 \qquad (11)$$

where $I_{corr\,(blank)}$ and $I_{corr\,(Inh)}$ are uninhibited and inhibited current densities respectively. Data in Table-5 shows that the inhibition efficiency increased with increasing the inhibitor concentrations[28].

Adsorption isotherm: The adsorption behaviour of the inhibitor molecules on metal surface can be applied to explain

TABLE-5
POTENTIODYNAMIC POLARIZATION PARAMETERS FOR MILD STEEL IN 1 N HCl
CONTAINING DIFFERENT CONCENTRATIONS OF *Musa acuminata* FLOWER EXTRACT

Concentration of extract (% v/v)	$-E_{corr}$ (V)	I_{corr} (mAmp/cm^2)	b_c (mV/dec)	b_a (mV/dec)	R_p (ohm cm^2)	IE (%) Tafel	IE (%) Linear
Blank	0.466	2887.00	258.78	206.34	8.204	–	–
0.05	0.455	267.30	170.74	80.24	8.267	90.74	0.76
0.10	0.465	185.60	195.78	72.73	11.045	93.57	25.72
0.50	0.479	101.70	212.32	69.66	12.069	96.48	32.02
1.00	0.482	67.65	202.91	68.40	12.851	97.66	36.16
1.50	0.483	42.83	172.43	70.38	13.403	98.52	38.79
2.00	0.484	29.88	158.97	79.57	22.362	98.97	63.31
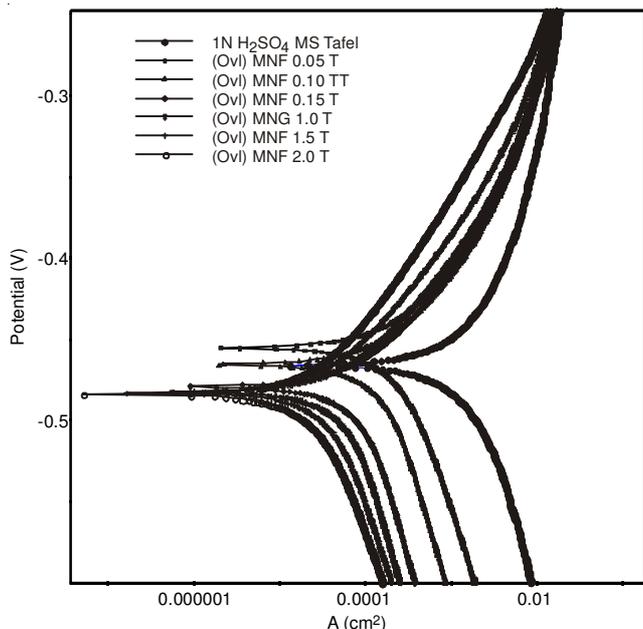
Fig. 4. Potentiodynamic polarization curves for mild steel in 1 N HCl solution in the absence and presence of different concentrations of *Musa acuminata* flower extract

Fig. 5. Langmuir adsorption isotherm plot for adsorption of different concentrations of *Musa acuminata* extract on the surface of mild steel in 1 N HCl at different temperatures
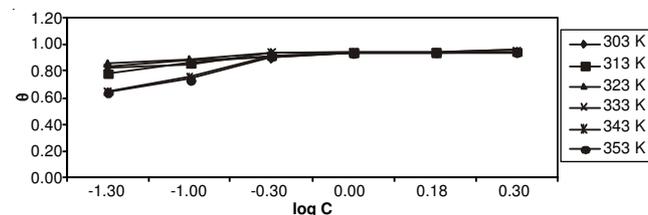
Fig. 6. Temkin adsorption plots for mild steel in 1 N HCl at different temperatures

the inhibition mechanism of MAF extract. Several adsorption isotherms can be used to study the adsorption behaviour of the inhibitor. The degree of surface coverage (θ) for different concentrations of inhibitor molecules in 1 N HCl was calculated from weight loss measurements using the equation,

$$\theta = \frac{W° - W}{W°} \times 100 \tag{12}$$

where W° and W are the weight loss in the absence and presence of the extract.

Data were tested graphically by fitting in Langmuir and Temkin isotherms. From the linear plots of $\log\left(\frac{\theta}{(1-\theta)}\right)$ *versus* log C and θ *versus* log C, it can be seen that the inhibitor obeys both Langmuir and Temkin isotherm (Figs. 5 and 6) indicating that the main process of inhibition involves the adsorption of the inhibitor on mild steel[34].

Activation energy: The nature of adsorption, the activation process and influence of temperature on the inhibition process give more information about the inhibition performance of the extract. Based on the temperature effect Rodovici classified inhibitors into three groups: (i) Inhibitors whose IE decreases with temperature increase and have greater E_a than

that of the uninhibited solution. (ii) Inhibitors whose IE do not change with temperature and the E_a does not change with presence or absence of inhibitors. (iii) Inhibitors whose IE increases with increase in temperature and E_a is found to be smaller for the uninhibited solution, which is characteristic of chemisorptions.

The effect of temperature on inhibition reaction is highly complex, because changes may occur on the metal due to rapid etching, rupture, desorption of inhibitor, decomposition and rearrangement of inhibitor[28]. The effect of temperature on the rate of corrosion was studied in the absence and presence of MAF extract. The activation parameter for corrosion process was calculated using the Arrhenius equation:

$$\log CR = \frac{-E_a}{2.303RT} + \log A \tag{13}$$

where CR is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor.

Fig. 7 represents linear plots of log CR *versus* 1/T for mild steel corrosion in 1 N HCl in the absence and presence of various concentration of MAF extract. The values of E_a were obtained from the slope of the Arrhenius plot and are presented in Table-6. Results show that E_a increases in the presence of the extract compared to the blank. The higher value of the activation energy in the presence of inhibitor is attributed to its physisorption while the opposite is the case with chemisorption[32].
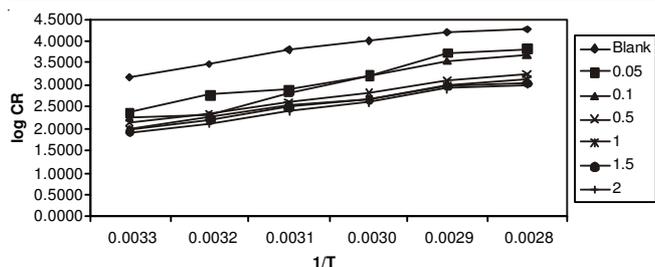
Fig. 7. Arrhenius plot for mild steel immersed in 1 N HCl solution in the absence and presence of *Musa acuminata* flower extract

TABLE-6 ACTIVATION ENERGY VALUES OF MILD STEEL CORROSION IN ACID MEDIUM IN ABSENCE AND PRESENCE OF MAF EXTRACT			
Conc.	E_a (kJ/mol)	Conc.	E_a (kJ/mol)
Blank	43.34	1.00	44.06
0.05	57.26	1.50	42.75
0.10	62.30	2.00	44.10
0.50	43.05	–	–

Thermodynamic parameters: The free energy of adsorption (ΔG°_{ads}) was calculated using the equation:

$$\Delta G^\circ_{ads} = -RT \ln 55.5 K_{ads}, \quad K = \left[\frac{\theta}{C(1-\theta)} \right] \quad (14)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature and the value of 55.5 is the concentration of water in solution[33].

The values of ΔG°_{ads} are listed in Table-7. The negative values for ΔG°_{ads} indicate that the inhibitor is spontaneously adsorbed on the metal surface by strong interaction between the inhibitor molecules and the mild steel surface. It has been reported that ΔG°_{ads} value upto 20 KJ/mol or lower indicates a physical adsorption while that more negative than -40 KJ/mol involves sharing or transfer of electron from the inhibitor molecules to the metal surface to form a chemisorptions by co-ordinate bond[35]. Table-7 summarized the values of ΔG°_{ads} range from -25 KJ/mol to -15 KJ/mol indicating the adsorption of inhibitor on the mild steel may be due to physisorption.

Values of other thermodynamic parameters like enthalpy of adsorption (ΔH°_{ads}) and entropy of adsorption (ΔS°_{ads}) also provide information about the mechanism of corrosion inhibition. The enthalpy ΔH°_{ads} and entropy ΔS°_{ads} adsorption on mild steel in 1 N HCl in presence of the inhibitor can be calculated from the basic thermodynamic equation (eqn. 9).

The negative sign of the ΔH°_{ads} indicates that the adsorption process is spontaneous while positive sign of ΔS°_{ads} shows a decrease in the system order[36].

SEM photographs of mild steel surface after immersion for 5 h in the presence and absence of inhibitor MAF extract are shown in Fig. 8A-B. The inhibited metal surface is smoother than the uninhibited surface indicating that corrosion rate is reduced to a very low value in the presence of the inhibitor. This may be due to adsorption of inhibitor molecules on the surface as a protective layer preventing acid attack and sequentially[33]. Energy dispersive X-ray spectroscopy (EDAX) was employed to investigate the composition of the corrosion scales in the case of mild steel immersed in (i) HCl (ii) 2 % v/v MAF extract. EDAX results for the mild steel exposed to MAF extract summarized in Table-8(A-C) indicate the presence of Si, Mn and Cu on the surface in addition to Fe and C as in mild steel (Figs. 9(A-B), 10 and 11). This can be attributed to the adsorption of nutrients from the MAF flower extract on the mild steel enhancing the inhibition properties through complex formation with the metal atoms[20].
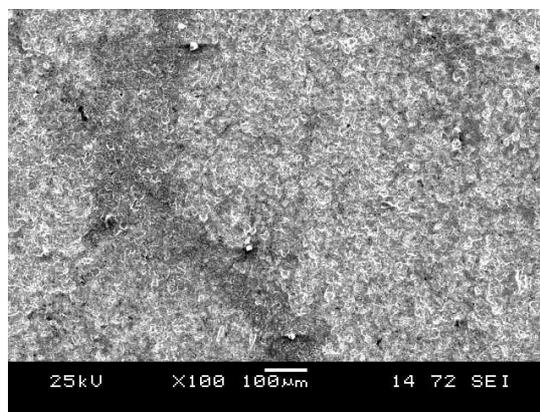
Fig. 8. (A) SEM image of mild steel in 1 N HCl medium
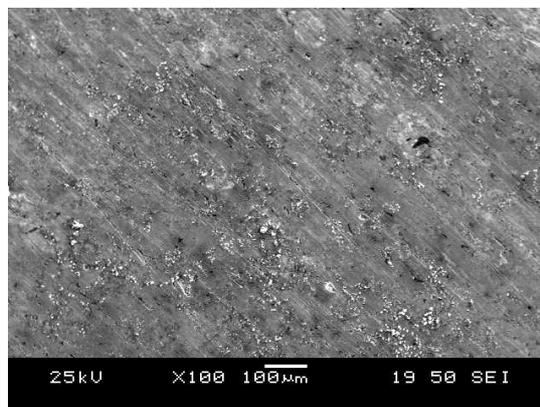
Fig. 8. (B) SEM image of mild steel 1 N HCl medium in presence of *Musa acuminata* flower extract

TABLE-7 THERMODYNAMIC PARAMETERS OF ADSORPTION FOR MILD STEEL IN 1 N HCl IN THE PRESENCE OF *Musa acuminata* FLOWER EXTRACT								
Conc. (% v/v)	ΔG (kJ /mol)						ΔS (kJ/mol)	ΔH (kJ/mol)
	303 K	313 K	323 K	333 K	343 K	353 K		
0.05	-21.82	-23.17	-24.42	-24.91	-24.92	-25.21	-0.0648	-2.8112
0.10	-20.92	-21.61	-23.89	-23.55	-23.42	-23.85	-0.0564	-4.3741
0.50	-17.38	-18.97	-20.01	-20.63	-20.78	-20.96	-0.0684	-2.6562
1.00	-16.61	-17.16	-18.15	-18.71	-19.83	-19.35	-0.0636	-2.5685
1.50	-16.01	-16.53	-17.58	-18.12	-18.67	-19.21	-0.0656	-3.8301
2.00	-15.28	-16.90	-18.24	-17.98	-18.52	-19.06	-0.0671	-4.3595

TABLE-8A
COMPOSITION OF MILD STEEL IMMERSED IN
ABSENCE AND PRESENCE OF MAF EXTRACT
REGARDING THE EDAX ANALYSIS

Sample	Element (%)				
	C	Fe	Si	Mn	Cu
Mild steel without inhibitor	9.20	90.80	–	–	–
Mild steel with MAF inhibitor	7.09	90.80	1.29	0.28	0.54

TABLE-8B
COMPOSITION OF MILD STEEL IMMERSED IN ABSENCE OF
MAF EXTRACT REGARDING THE EDAX ANALYSIS

Element	Net counts	Weight (%)	Atom (%)
C	1024	9.20	32.03
Fe	148796	90.80	67.97
Total	–	100.00	100.00

TABLE-8C
COMPOSITION OF MILD STEEL IMMERSED IN PRESENCE
OF MAF EXTRACT REGARDING THE EDAX ANALYSIS

Element	Net counts	Weight (%)	Atom (%)
C	664	7.09	25.93
Si	3302	1.29	2.02
Mn	441	0.28	0.23
Fe	131252	90.80	71.45
Cu	443	0.54	0.37
Total	–	100.00	100.00
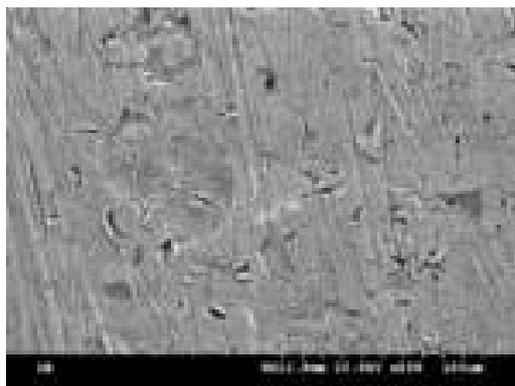
(a)
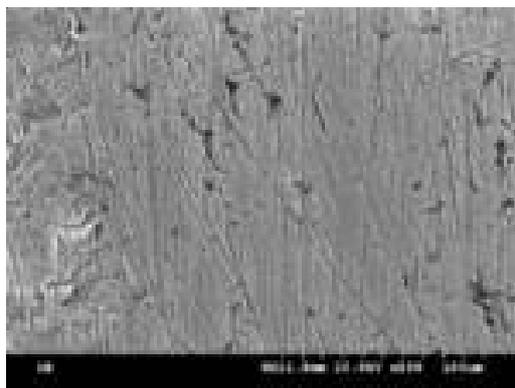
(b)

Fig. 9. EDAX micrograph of mild steel (a) without inhibitor (b) with inhibitor

Fig. 10. EDAX spectra of mild steel in 1 N HCl solution
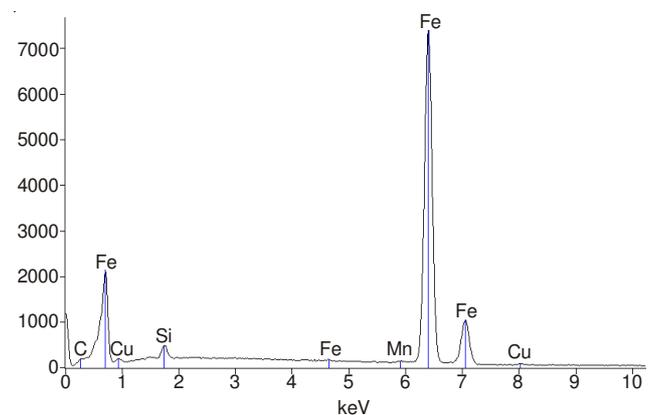
Fig. 11. EDAX spectra of mild steel in presence of *Musa acuminata* flower extract in 1 N HCl

Characterization of the flower extract: Studies on the phytochemical constituents of *Musa acuminata* flowers show that it contains various phytochemical and antioxidants. Analysis revealed that the banana flower contains crude chemical constituents of amino acids (0.033 %) and terpenoids (1.7 %), flavonoid (0.038 %). The antioxidant activity of flower extract was determined using the 1-diphenyl-2-picrylhydrazyl (DPPH) free radical scavenging assay (67.43 %). The study shows antioxidant activity in banana flowers which may be due to potential source of natural antioxidants[23,37]. The natural flavonoids have in their structure heterocyclic oxygen rings and the antioxidative activity stops the oxidation and corrosion, the deterioration process and discoloration[20].

Mechanism: Potentiodynamic polarization and EIS measurement clearly depict that corrosion of mild steel in 1 N HCl is retarded in the presence of MAF extract. The results clearly showed that the inhibition mechanism involves blocking of mild steel surface by inhibitor molecules by adsorption.

Adsorption of inhibitor involving organic molecules at the metal/solution interface may take place by four methods. (i) Electrostatic attraction between charged molecules and the charged metals. (ii) Interaction of unshared electron pairs in the molecule with the metal. (iii) Interaction of π electron with the metal. (iv) A combination of all the above.

Inhibition efficiency depends on the number of adsorption sites, their charge density, molecular size, heat of hydrogenation, mode of interaction with metal surface and formation of metallic complex. Physisorption requires the presence of electrically charged metal surface, charged species in the solution, presence of metal with vacant low-energy electron orbital and inhibitor molecules with lone pair of electrons[38].

The nutrients of the inhibitor may become cations in the acid medium as shown by the equation and get attached to the mild steel surface which is positively charged in HCl medium by electrostatic force of attraction between anion (Cl⁻) and cation (protonated MAF extract). The adsorption of MAF extract on mild steel surface may also take place by partial transfer of electron from the polar atom (N atom and π electrons of the double bond) of MAF extract.

$$\text{MAF extract} + nH^+ \leftrightarrow [MAF]^{n+} \qquad (15)$$
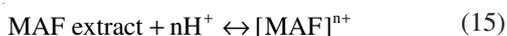
As corrosion begins, the cation may become attached to anodic sites and adsorption of extract on the metal surface can occur directly *via* donor-acceptor interactions between the π electrons of the heterocyclic compound and the vacant 'd' orbital of iron surface atom thereby inhibiting corrosion[21,39].

Besides the physical adsorption, MAF extract may be adsorbed on the metal surface *via* the chemisorptions mechanism, involving to the co-ordinate bonds that may be formed between the lone pair of the unprotonated N atoms and the empty orbital of Fe atom which enhanced the condensation intension between the inhibitor molecule and electrode surface[29].

Conclusion

The present study of corrosion of mild steel allows the following conclusions to be drawn: Flower extract of *Musa acuminata* (MAF) served to inhibit the corrosion of mild steel in 1 N HCl. The inhibition efficiency increases and corrosion rate decreases with increase in inhibitor concentration. The flower extract of *Musa acuminata* was an excellent corrosion inhibitor for mild steel showing a maximum efficiency of 97.16 % in 1 N HCl at 5 h in 2 % v/v of MAF extract. The adsorption of MAF extract is a spontaneous process and obeys Langmuir and Temkin adsorption isotherm. The activation energy, E_a, values show the temperature dependence of the inhibitor efficiency. The negative value of ΔG°_{ads} and ΔH°_{ads} indicate the physisorption nature of adsorption by the inhibitor. EIS spectra exhibit one capacitive loop which indicates that the corrosion reaction is controlled by charge transfer process. Polarization curve recorded shows that the flower extract of *Musa acuminata* is a mixed type of inhibitor. Inhibitor showed maximum efficiency of 98.97 % (potentiodynamic studies) and 96.58 % (impedance studies) at 2 % v/v MAF extract. Decrease in I_{corr} and C_{dl} values and increase in R_{ct} values confirmed the inhibition action of the inhibitor, due to increased adsorption layer. The adsorption of MAF involves electrostatic attraction sharing electrons between N, O atoms and Fe, donor-acceptor interactions between π electrons of conjugated double bonds. Surface studies involving SEM and EDAX confirmed the efficiency of the flower extract as corrosion inhibitor for mild steel. The inhibition efficiencies obtained by conventional weight loss method and electrochemical measurements were quite comparable.

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