Research Article

Musa acuminata Bract Extract as Corrosion Inhibitor for Mild Steel

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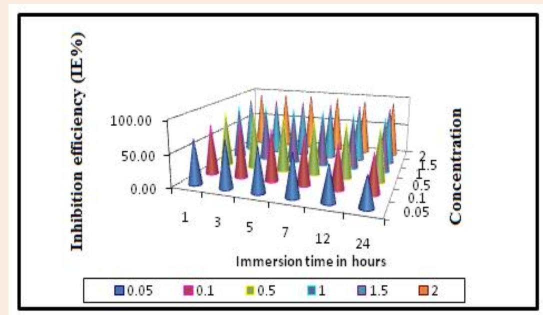
Abstract

The anticorrosive efficiency of bract extract of *Musa acuminata* 'Nendran' [MAN (B)] in 1N sulphuric acid on mild steel surface was investigated by weight loss, potentiodynamic polarisation and electrochemical impedance spectroscopy methods. Weight loss measurement results revealed that corrosion inhibition increased with increase in inhibitor concentration and was about 93.09 in 2% v/v concentration of bract extract. Polarization measurements indicated that the extract acted as mixed type inhibitor. Electrochemical impedance results also showed that the MAN (B) extract increased the resistance of mild steel towards corrosion. Scanning electron microscopic study offers a confirmatory evidence for the protection of mild steel by the inhibitor through adsorption. The studies revealed the corrosion combating potential of bract extract which follows Langmuir adsorption isotherm. The adsorption characteristic of phytochemicals of *Musa acuminata* bract on to the surface of the mild steel was studied to assess the mechanism of corrosion inhibition.



Keywords: *Musa acuminata*, Bract extract, Mild steel, Sulphuric acid, Langmuir adsorption

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Introduction

Corrosion is an irreversible interfacial reaction of a material with its environment which results in consumption of the material or in the dissolution of the material into the components of the environment [1, 2]. With the development of technology, there is an increasing use of metals in all fields of technology. Rare and costly metals require special protection. Increasing pollution of air and water result in more corrosive environments and as a result the operating industrial equipments may fail in a catastrophic manner due to corrosion. It is thus necessary to offer more attention to metallic corrosion because it affects safety. The cost of corrosion is also of major economic consequence as it leads to increased losses in the industrial sectors [3, 4].

Among the different corrosion control methods, the most important, convenient and practicable method is use of corrosion inhibitors. Inhibitors slow the corrosion processes. Cost, toxicity, availability and environmental friendliness are of considerable importance in choosing the indicators [5]. Most of the natural products studied as inhibitors have been reported to be efficient inhibitors. Mostly the nitrogenous heterocycles, tannins, oxygen containing heterocycles like flavones, coumarins, anthocyanins and flavonoids present in plant materials are reported to be responsible for inhibitor action [6, 7].

Review of literature shows that the selected plant material in the present study has not been studied as corrosion inhibitor for mild steel in 1N sulphuric acid. In the present study inhibitive efficiency of sulphuric acid extract of *Musa acuminata* bract is studied using weight loss, potentiodynamic polarisation, electrochemical impedance and surface analysis studies.

Experimental

Materials

Properties and Applications of Musa acuminata bract

Musa is one of the three genera in the family of *Musaceae*. It includes banana and plantains. One of the cultivar varieties is *Musa acuminata* 'Nendran'. On maturing, a true stem or growing point emerges as banana blossom (inflorescence) from the centre of the tightly rolled bunch of leaves. The banana inflorescence is an elongated, plump, dark purple bud. Group of flowers are arranged radially on the stem in nodal clusters. Each flower cluster is borne on a prominence on the stem bearing the fruit and covered by bract. Bracts lift from the first hand in 3 to 10 days. The bracts are soon shed and fully grown fruits in each cluster become a hand of bananas (Figure 1). Banana flowers are treated in several cuisines as vegetables. Banana flower are considered to be good source of vitamin A and C. It is traditionally believed to be beneficial as a lactating agent and help to relieve painful menstruation [8].

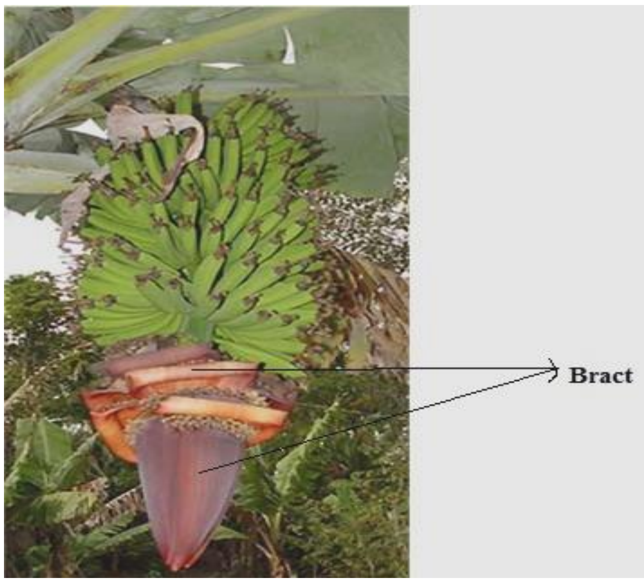


Figure 1 *Musa acuminata* 'Nendran' fruit bunch with inflorescence

Previous research on preliminary phytochemcial screening of dried leaves and fruit peels of *Musa paradisiaca* revealed the presence of some glycosides, anthocyanins, tannins, flavanoids and carbohydrates [9-11]. No research has been reported on the phytochemical screening of banana flowers except a quantitative study on saponins and flavanoids [12] and later phenolic content by Loganayaki et al [13]. The bract part of *Musa paradisiaca* was reported to contain anthocyanins such as delphinidin, pelaragonidin, peonidin and malvidin [14, 15]. Total phenolic content in bract was reported as the lowest compared to other parts such as rhizome, fruit peel, ovary, petiole, pseudo stem and leaves [16].

Methods

Preparation of bract extract

Matured *Musa acuminata* inflorescence was harvested from the banana farm in Thirumalayampalayam, Coimbatore, Tamilnadu, India. The bracts are gently peeled off, washed, shade dried (Figure 2) and powdered in an electronic blender. 25g of this powder was refluxed with 500 ml of 1N H_2SO_4 for 3h and left overnight to extract the phytonutrients. It was filtered and filtrate made up to 500 ml using 1N H_2SO_4. From this 5% stock solution, the required concentration was prepared by diluting it [17].

Preparation of experimental specimen

The mild steel coupons of size 5x1 cm were degreased with acetone to remove grease, oil and dust, washed with distilled water and dried. The coupons were then mechanically polished with 400 and 600 grade emery papers, cleaned, dried and then stored in desiccators. The prepared mild steel specimens were weighed in an electronic balance and immersed in 100 ml of 1N H_2SO_4 with various concentration of bract extract (0.05, 0.10, 0.50, 1.00, 1.50, 2.00 % v/v) and without the bract extract (blank). After 1h of immersion in the test solution, the specimens were removed, washed with distilled water, dried and weighed.

Figure 2 Shade drying of *Musa acuminata* bracts

The experiment was carried out at various immersion periods (1h, 3h, 5h, 7h, 12h, 24h) for various concentrations of the inhibitor at 303 K. Corrosion inhibition studies were also carried out at temperature range 303 – 353 K in the absence and presence of MAN(B) extract in 1N H_2SO_4 for 1h duration [18].

From the weight loss, percentage inhibition was calculated using the following formula (1):

$$\text{Inhibition efficiency (IE \%)} = W_{blank} - W_{inh} / W_{blank} \times 100 \quad \rightarrow (1)$$

where W_{blank} and W_{inh} are weight loss without and with bract extract respectively.

Electrochemical study

Potentiodynamic polarisation

Potentiodynamic polarization studies were carried out using frequency response analyzer PARSTAT 2273 (Princeton Applied Research USA) and IBM personal computer to record Tafel polarisation curve and Nyquist impedance curve. The polarisation measurements were carried out to evaluate the corrosion current (I_{corr}), corrosion potential (E_{corr}) and Tafel slopes b_a and b_c. Experiments were carried out in a conventional three electrode cell assembly. Mild steel rod of 15 cm and 5 mm diameter mounted on a Teflon leaving 0.19625 cm^2 of surface area exposed to solution was used as working electrode. It was polished with 120, 200, 400, 600, 800, 1000 grade emery papers, cleaned with acetone, washed with distilled water and dried at room temperature, before it is immersed in test solution. A rectangular platinum foil and calomel electrode served as auxiliary and reference electrodes respectively. A time interval of 10 min was allowed for each experiment to attain the steady state open circuit potential. The measurements were carried out in the frequency range of 10^6 – 10^{-2} Hz at the open circuit potential by superimposing a sinusoidal AC signal of small amplitude 10 mV. The data acquisition was performed using the Power Suite software and analysed using Zsimpwin software (version 3.21) to evaluate the corrosion kinetics parameters, such as I_{corr}, E_{corr}, Tafel slopes b_a and b_c [19].

From the polarisation curves, Tafel slopes, corrosion potential and corrosion current were analysed using computer software [20]. The inhibitor efficiency by Tafel method was calculated using equation (2):

$$\text{Inhibitor Efficiency (\%)} = \frac{I_{corr}\text{ (blank)} - I_{corr}\text{ (Inh)}}{I_{corr}\text{ (blank)}} \times 100 \quad \rightarrow (2)$$

where,

I_{corr} (blank) = Corrosion current without inhibitor
I_{corr} (Inh) = Corrosion current with inhibitor.

Electrochemical Impedance spectroscopy (EIS)

The electrochemical AC-impedance measurement was carried out in the three electrode cell assembly as that used for potentiodynamic polarisation studies. The impedance measurements were made at corrosion potentials 1.66 mVs^{-1}. 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 Z' against Z" were made. From the plot, the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated using the "Z" view software. Impedance measurements were carried out for mild steel in 1N sulphuric acid without and with inhibitors for the selected concentration [21].

The inhibitor efficiency (IE %) by linear polarization method was calculated using equation (3) :

$$\text{Inhibitor Efficiency (\%)} = \frac{R_{ct}\,(\text{Inh}) - R_{ct}\,(\text{blank})}{R_{ct}\,(\text{Inh})} \times 100 \quad \rightarrow (3)$$

where,

R_{ct} (inh) = Charge transfer resistance with inhibitor
R_{ct} (blank) = Charge transfer resistance without inhibitor

Surface examination studies

Surface analysis of mild steel specimens reflects the changes that occur during the corrosion of mild steel in the absence and presence of the inhibitor. The inhibitive action of plant extracts on mild steel corrosion was investigated by scanning electron microscope (SEM) technique. The mild steel specimens were immersed in 1N sulphuric acid solution in the absence and presence of 2% v/v concentration of the inhibitor for a period of 3h at 303K. The specimen was removed after the specified time, washed carefully with distilled water without disturbing the surface and dried. SEM micrograph of the samples were taken to examine the nature of corrosion product formed on the surface of mild steel specimens using JOEL SEM model JSM 6360 at Metallurgy department, PSG College of technology, Coimbatore, India.

Results and Discussion

Weight loss method

Effect of inhibitor concentration

Figure 3 shows the IE of various concentration of inhibitor on mild steel in sulphuric acid. The weight loss method of monitoring corrosion is useful because of its simple application and high reliability. Maximum inhibition efficiency was shown at 2% v/v concentration. Further increase in inhibitor concentration did not show significant increase in efficiency. Increase in IE with increase in concentration indicates strong adsorption of phytoconstituents present in the bract extract on the surface of mild steel which makes a barrier for mass and charge transfer and protects the metal surface from corrosion [21]. It is observed that there was marked reduction in the corrosion rate of mild steel even for a concentration of 0.05% v/v.

Effect of immersion time

Table 1 gives percentage inhibition efficiency obtained in 1N H_2SO_4 in absence and presence of MAN (B) extract at 303K for immersion period from 1h to 24h. The inhibition efficiency increases with increase in concentration of the inhibitor irrespective of the time of immersion. Maximum IE of 93.09% was observed for 2% v/v concentration at 5h of immersion period. Immersion for a longer period leads to desorption of the adsorbed phytochemical constituents [22].

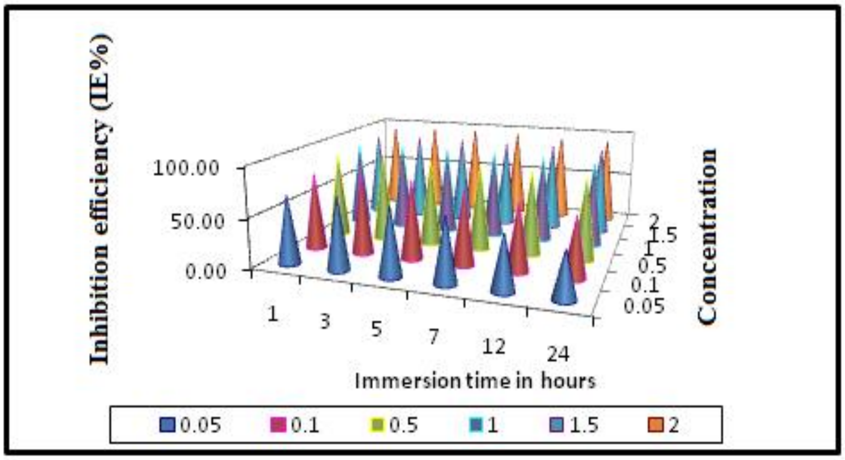


Figure 3 Influence of immersion time on IE % of MAN (B) extract in 1N H_2SO_4 acid

Table 1 IE of MAN (B) extract in 1N H_2SO_4 acid of various concentration and immersion period

Conc. of extract (% v/v)	**Inhibition Efficiency (IE %)**					
	1h	**3h**	**5h**	**7h**	**12h**	**24h**
0.05	74.56	70.86	60.20	59.66	50.40	33.51
0.10	80.04	79.86	72.89	70.38	65.37	54.27
0.50	89.24	89.24	88.46	86.68	85.98	82.54
1.00	91.00	91.00	90.20	90.59	89.63	87.66
1.50	91.98	91.95	91.79	92.70	91.74	90.82
2.00	92.56	92.95	93.09	92.96	91.92	91.64

Effect of temperature

To evaluate the stability of the adsorbed film on the mild steel, weight loss measurement was carried out over a range of 303 K – 353 K in presence and absence of the inhibitor for an immersion period of 1h. The results obtained are listed in Table 2. The IE increases up to 323 K and then decreases thereafter. At elevated temperature the time lag between adsorption and desorption decreases as a result the rate of dissolution of mild steel increases and hence the inhibition efficiency decreases. Also with increased desorption of inhibitor molecules at higher temperature, more surface area of mild steel comes in contact with the acid environment, resulting in decrease in IE with increase in temperature [23].

Adsorption isotherm

Basic information about the interaction between the inhibitor and mild steel surface can be obtained from the adsorption isotherms. The extent of corrosion inhibition depends on the surface condition and mode of adsorption of the inhibitor. The surface coverage (θ) values for various concentrations of the inhibitor in sulphuric acid medium were evaluated from the weight loss data. A plot of C/θ against C generated a straight line (Figure 4) with slope close to unity and regression coefficient greater than 0.9 indicating strong adherence to Langmuir adsorption isotherm [24].

Table 2 Effect of temperature on mild steel corrosion in 1N H_2SO_4 in absence and presence of MAN (B) extract

Conc. of extract (% v/v)	Inhibition Efficiency (IE %)					
	303 K	313 K	323 K	333 K	343 K	353 K
0.05	74.56	63.43	68.04	63.23	46.74	52.83
0.10	80.04	76.09	77.04	69.27	51.67	54.79
0.50	89.24	78.32	84.04	83.20	76.03	79.59
1.00	91.00	87.42	87.75	85.75	84.83	81.63
1.50	91.98	89.92	92.04	89.96	86.06	85.41
2.00	92.56	94.65	95.83	90.52	88.61	86.85

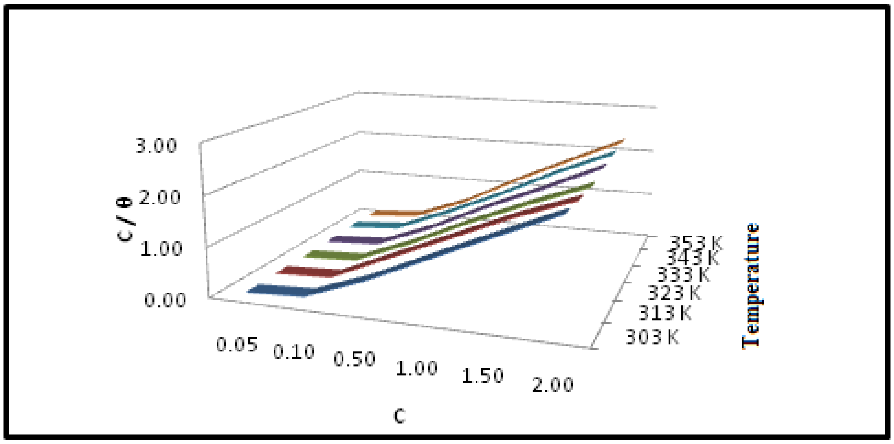


Figure 4 Langmuir isotherms for adsorption of MAN (B) extract in 1N H_2SO_4 on mild steel surface

Electrochemical study
Potentiodynamic polarisation

The cathodic and anodic polarisation curves recorded for mild steel in 1N H_2SO_4 solutions without and with various concentration of MAN (B) extract is illustrated in Figure 5. Electrochemical corrosion kinetic parameters obtained by Tafel extrapolation method are given in Table 3. From the shape of the polarisation curve (Figure 5), it can be seen that both anodic as well as cathodic reactions are inhibited, indicating that MAN (B) acts as mixed-type inhibitors. The addition of MAN (B) extract to sulphuric acid solution therefore reduces the anodic dissolution of metal and also retards the cathodic evolution reaction. It can be seen from the polarisation results that the corrosion current density (I_{corr}) decreased with the increase in inhibitor concentration, due to the increase in the blocked fraction of the metal surface by adsorption. The polarisation resistance (R_p) values were determined from the corrosion potential. It was found that R_p values increase with increase in MAN (B) extract concentration [25]. The inhibition efficiencies calculated from the corrosion current density and the polarisation resistance increased with the inhibitor concentration reaching a maximum value at 2% v/v.

Electrochemical impedance spectroscopy (EIS)

The corrosion behaviour of mild steel in 1N H_2SO_4 solution in the presence of MAN (B) was investigated by the EIS method at 303 K (Figure 6). It is apparent that the impedance response of mild steel in uninhibited H_2SO_4 solution has significantly changed after addition of MAN (B) in the corrosive solution. The diameter of the semicircle increased with increasing the concentration. This confirms that the impedance of inhibited substrate increases with the concentration of MAN (B) in 1N H_2SO_4. The parameters deduced from the fit of Nyquist diagram for 1N H_2SO_4 medium containing various concentrations of MAN (B) are given in Table 4. Addition of MAN (B) increases C_{dl} value indicating reduction of surface inhomogeneity due to the adsorption of plant extract molecules. Capacitance values decreases on increasing the MAN (B) concentration indicates reduction of charges accumulated in the double layer due to formation of adsorbed plant extract layer. The charge transfer resistances of double layer (R_{ct}) increases on increasing the MAN(B) concentration indicating that increase in concentration of bract extract decreases corrosion and increases inhibition [26]. Maximum corrosion inhibition efficiency of 95.03% (C_{dl}) and 91.27% (R_{ct}) was noticed for 2% v/v bract extract.

Table 3 Potentiodynamic polarization parameters for mild steel in1N H_2SO_4 in absence and presence of MAN (B)

Conc. of extract (% v/v)	**$-E_{corr}$ (V vs. SCE)**	**Tafel slope**		**I_{corr} µAmp/cm^2**	**IE % Tafel**	**R_p Ohmcm^2**	**IE % Linear**
		b_a mV/dec	**b_c mV/dec**				
Blank	0.491	81.30	180.69	1005.00	-	3.30	-
0.05	0.458	86.49	224.32	414.90	58.72	5.10	35.29
0.50	0.466	70.28	224.52	380.70	62.12	7.12	53.65
1.00	0.461	58.30	205.98	247.80	75.34	12.67	73.95
2.00	0.452	40.51	185.19	52.88	94.74	15.13	78.19

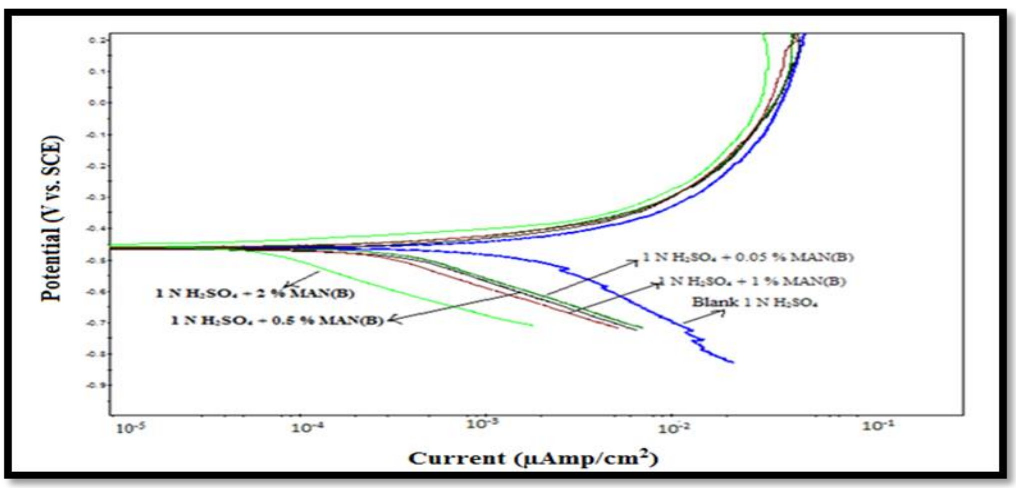


Figure 5 Potentiodynamic polarization curves for mild steel in 1N H_2SO_4 without and with various concentrations of MAN (B) extract

Surface examination studies

SEM images of the mild steel specimens exposed to 1N H_2SO_4 at 303 K for 3h in the absence and presence of 2% v/v concentration of the MAN (B) extract are shown in Figures 7 a, b, c. The parallel features on the polished mild steel surface (Figure 7a) before exposure to the corrosive acid medium, are associated with polishing scratches. Micrograph Figure 7b revealed that the mild steel surface was strongly damaged in absence of inhibitor. Figure 7c clearly showed that the mild steel surface was covered with the protective layer formed by the inhibitor which prevents the metal from further attack of acid media thus inhibiting corrosion [27].

Table 4 Impedance parameters for mild steel in the absence and presence of MAN (B) in 1N H_2SO_4

Conc. of extract (% v/v)	**C_{dl} µFcm^{-2}**	**R_{ct} Ohmcm^2**	**IE % C_{dl}**	**R_{ct}**
Blank	11.07 x 10^{-5}	18.25	-	-
0.05	1.534 x 10^{-5}	44.23	86.14	58.74
0.50	1.481 x 10^{-5}	47.21	86.62	61.34
1.00	1.359 x 10^{-5}	60.95	87.72	70.06
2.00	5.515 x 10^{-6}	209.00	95.03	91.27

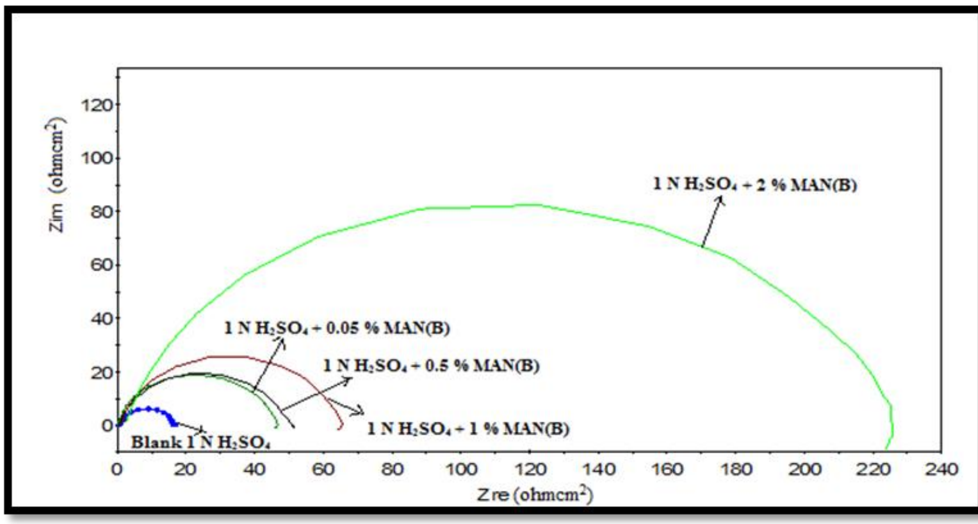
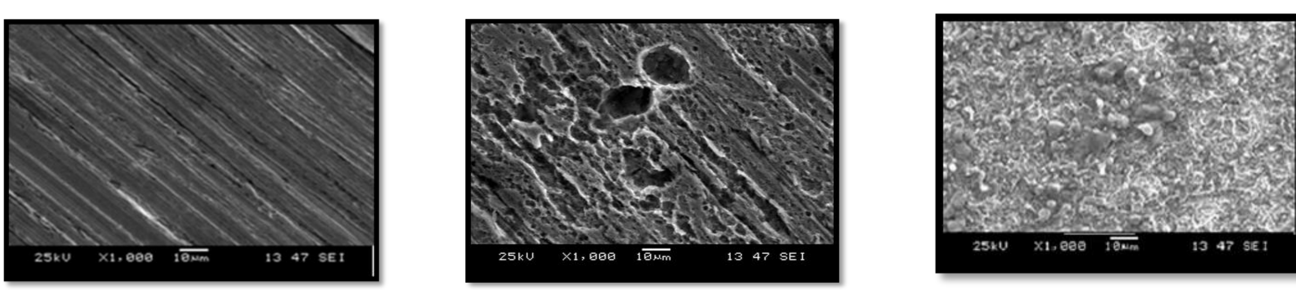


Figure 6 Nyquist plots of mild steel in 1N H_2SO_4 without and with various concentration of MAN (B) at 303 K



(a) (b) (c)

Figure 7 (a) Polished mild steel surface **(b)** Mild steel surface exposed to 1N H_2SO_4 **(c)** Mild steel surface exposed to 1N H_2SO_4 + MAN(B) extract

Proposed mechanism for inhibition by *Musa acuminata* bract extract

The mechanism of inhibition can be understood by knowing the mode of interaction of the inhibitor molecules with mild steel surface. Inhibitors function by adsorption and/or hydrogen bonding to the metal. Adsorption process can be governed by various parameters. This depends on the chemical composition and structure of the inhibitor, the nature of the metal surface, and the properties of the medium. Structural and electronic parameters like functional group, steric and electronic effects may also be responsible for the inhibition efficiency of any inhibitor, that is, the adsorption mechanism. The compounds have to block the active corrosion sites on the metal surface and hence the adsorption occurs by the bonding of the free electrons of inhibitor with the metal.
The bract extract may constitute organic compounds containing (i) lone pair of electrons present on a hetero-atom (eg. N, S, P, O) (ii) pi-bond (iii) triple bonds (eg. cyano groups) and (iv) heterocyclic compounds such as pyridine ring pyrrole, imidazole etc. Phytochemical analysis of *Musa acuminata* bract showed the presence of alkaloids, flavonoids, saponins, tannins, terpenoids, coumarins, glycosides, total phenols and steroids. These compounds possess hetero atoms such as O and N which strengthen their adsorptive property over mild steel surface. The inhibiting influence of these molecules may be attributed to their adsorption through the NH, C=O, OH, COOH etc. groups and also may be due to the presence of pi electrons in the rings. These organic molecules get physisorbed on the metal surface forming a protective film and hence the anti-corrosive behaviour [28].

Conclusion

Musa acuminata bract extract acts as efficient corrosion inhibitor on mild steel in 1N H_2SO_4 acid solution. Inhibition efficiency increases with inhibitor concentration and the maximum inhibition efficiency was 93.09% at 2% v/v concentration of bract extract. Temperature effect shows that *Musa acuminata* exhibits efficiency upto 323 K. Potentiodynamic polarisation studies indicated that the studied bract extract affected both anodic and cathodic reactions by blocking the active sites of mild steel surface and are of mixed type inhibitor. Results obtained in weight loss methods (non-electrochemical methods) are in good agreement with potentiodynamic polarisation and impedance methods (electrochemical methods). Corrosion inhibition efficiency can be attributed to adsorption of the various phytochemicals present in the bract which is revealed by SEM studies. The nature of the adsorption of MAN (B) extract on the mild steel surface was evaluated as physisorption.

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