



Corrosion Inhibition Studies of Mild Steel in Acid Medium Using *Musa Acuminata* Fruit Peel Extract

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Abstract: The inhibition effect of unripe fruit peel extract of *Musa acuminata* (Cultivar variety – Nendran) (MNP) on corrosion of mild steel in 1 N HCl has been investigated by weight loss and electrochemical impedance spectroscopy (EIS) with various concentrations of the extract. The effect of temperature on the corrosion inhibition of mild steel in the temperature range of 30 °C – 80 °C was carried out. The results indicate that MNP extract act as an effective inhibitor in the acid environment and is of mixed type inhibitor having efficiency as high as 96% at 2% inhibitor concentration. The inhibition efficiency of MNP extract increases with the increase of concentration but decreases with the increase in temperature. The inhibitor achieves its inhibition by physical adsorption of nutrients of the peel extract on the surface of the mild steel. The experimental data revealed that the adsorption occurred according to the Langmuir and Temkin adsorption isotherm.

Keywords: Plant extract, Corrosion inhibitor, Mild steel, Weight loss, Potentiodynamic Polarization, Adsorption.

Introduction

An antique fruit crop of the world, known as ‘Apple of the paradise’ botanically named as *Musa acuminata* (Nendran), cheapest and plentiful fruit, used widely as food without apparent toxic effect, having antimicrobial and antioxidant activity contains starch, fructosans, phenolic acids, anthocyanins, terpenoids, sterols, polyphenols, gallic acid and dopamine¹⁻⁵. The peel of the fruit contains beta sitosterol, stigmasterol, campesterol, cycloeucaleanol, cycloartanol and 24-methylene cycloartanol^{6,7}. The natural flavonoid present in banana exhibits an antioxidative activity that stops oxidation and corrosion, the deterioration process and discoloration⁸.

Corrosion is gradual destruction of a material because of its reaction with environment. Both direct and indirect losses due to corrosion are huge. The control of corrosion is thus primarily an economic problem. Corrosion inhibitors reduce the rate of either anodic oxidation or cathodic reduction or both^{9,10}.

An attempt to find corrosion inhibitors that are environmentally safe and readily available has been a growing trend in the use of natural products such as leaves, seeds, flowers and fruits extract as corrosion inhibitors for metals in acid cleaning processes¹¹⁻¹³. Several natural products like *Bauhinia purpurea*¹⁴ (leaves), *Uncaria gambir*⁸ (plant), *Azadirachta indica*¹⁵ (leaves, seeds, roots), *Aloe vera*¹⁶ (leaves), *Phyllanthus amarus*¹⁷ (leaves and seeds), *Occimum viridis*¹⁸, *Zenthoxylum-alatum*^{19,20} (fruit), *Musa sapientum*²¹ (peel), Green tea²² (leaves), *Theobroma cacao*, *Cola acuminata*²³ (leaves), *Hibiscus sabdariffa*²⁴, *Oxandra asbeckii*²⁵ and *Citrus paradisi*²⁶ (juice) were reported as effective corrosion inhibitors in acid medium.

The banana fruit Nendran also called as French plantain, a popular variety in Kerala, India, is relished as a fruit as well as used for preparing juice, healthy food powder, chips *etc.* Matured fruit slices are made into chips by frying in edible oil after dipping in brine, while the peels are used as fodder for the cattle. The present study makes use of the fruit peels which are available in plenty.

The study examines the action of unripe *Musa acuminata* fruit peel extract as corrosion inhibitor of mild steel in acid medium with various concentrations and temperature. The kinetics of corrosion of mild steel in acid medium has been identified by weight loss and electrochemical impedance spectroscopy methods.

Experimental

Inhibitor preparation

The peels of *Musa acuminata* fruit were collected from the chips manufacturing shops of Coimbatore city, dried and powdered. About 12.5 g of the powder was refluxed with 250 mL of 1 N HCl for about 3 hours and was allowed to stand overnight. The resultant solution was filtered and the filtrate was made up to 250 mL. From this 5% stock solution of the extract, different concentrations of the inhibitor solution like 0.005, 0.01, 0.05, 0.10, 0.50, 1.0, 1.5, and 2.0 % v/v were prepared.

Specimen preparation

For weight loss method mild steel coupons of dimension 1 x 5 x 0.2 cm with a small hole on the upper part to facilitate suspension of the coupons in the test solutions were used. The specimens were degreased with acetone and pickled with concentrated hydrochloric acid. The surface of the specimens were mechanically polished using SiC emery papers of grades 400 and 600, washed with distilled water, dried at room temperature and stored in a desiccator.

For electrochemical polarization and impedance measurements mild steel rod of 15 x 0.5 cm were used. These rods were mechanically polished using different grades of SiC emery paper, repeatedly rinsed with distilled water and dried before use.

Weight loss method

Effect of concentration

The prepared specimens in duplicate were suspended from glass hook in 100 mL of the test solution, with and without the extracts of different concentration for 1, 2, 3, 4, 5, 6, 7, 12 and 24 h at room temperature. The weight of the specimens before and after immersion was

determined using an analytical balance of 0.0001 mg accuracy. Inhibition efficiency of the mild steel was determined using the average of the duplicate value using the relation

$$IE \% = \frac{W_1 - W_2}{W_1} \times 100$$

Where, W_1 and W_2 are weight loss of the mild steel without and with the inhibitor respectively.

Effect of temperature

The polished and pre-weighed specimens in duplicate were suspended in 100 mL of the test solution without and with the addition of different concentrations of the peel extract for 1 h in the temperature range of 30-80 °C using thermostat. After the corrosion test, the specimens were washed with distilled water, dried and weighed. From the weight loss the inhibition efficiency (IE %) was calculated.

Electrochemical measurements

A three electrode cell assembly of borosil glass consisting of a mild steel rod of size 15 X 0.5 cm as working electrode (WE), a large area platinum mesh of negligible impedance as counter electrode (CE), and a saturated calomel electrode as reference electrode (RE) containing 100 mL of the test solution was used for electrochemical measurements at 30 °C.

Potentiodynamic polarization studies

Potentiodynamic polarization studies were done using computer controlled PARSTAT 2273 – Advanced Electrochemical System. Before recording the polarization curves the mild steel rod as a working electrode was immersed in the test solution for 10 minutes to reach saturation. The potential was changed with the speed of 2 MHz to 100 mHz min⁻¹. From polarization measurement, the corrosion current (I_{corr}), corrosion potential (E_{corr}) and anodic (ba) and cathodic (bc) Tafel slopes were determined. The percentage inhibition efficiency (η) was calculated from,

$$\eta = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100$$

Where, I_{corr} and $I_{corr(inh)}$ are corrosion current density without and with inhibitor respectively.

Electrochemical impedance spectroscopy (EIS)

EIS study enables us to understand the various processes that take place on the metal-electrolyte solution interface, adsorption-desorption of the reaction intermediates. The Nyquist plots are obtained by measuring AC impedance and Tafel plot using polarization data. The EIS experiments were conducted using the same setup as used in the polarization method using frequency range 2 MHz to 100 mHz with AC amplitude of 10 mv. The real (Z') and imaginary (Z'') impedance values were measured for various frequencies. The charge transfer resistance values (R_{ct}) obtained by plotting Z' vs. Z'' were used to calculate the percentage inhibition efficiency from

$$IE \% = \frac{R_{ct}^0 - R_{ct}}{R_{ct}^0} \times 100$$

Where, R_{ct} and R_{ct}^0 are charge transfer resistance values with and without inhibitor.

Results and Discussion

Weight loss method-effect of concentration

The inhibition efficiency of mild steel exposed to different concentration of MNP extract in 1 N HCl at various immersion periods at 30 °C are presented in the Table 1 and Figure 1. The corrosion inhibition efficiency increased with the increase in concentration of the peel extract¹³. Maximum efficiency of 96.08 % was achieved with 2% of MNP extract at 5 hours of immersion at 30 °C. The increase in inhibition efficiency may be attributed to the increase in number of adsorption of nutrients on the surface of mild steel which makes a barrier for mass and charge transfer and prevent further corrosion¹².

Table 1. IE % of MNP extract on mild steel in 1 N HCl at different concentration and different immersion periods

Conc. of extract, % v/v	Immersion time in hours								
	1	2	3	4	5	6	7	12	24
0.005	68.21	56.48	42.70	46.15	53.64	47.23	44.05	50.30	53.47
0.01	77.96	74.27	64.06	68.75	61.55	62.57	64.11	63.45	62.54
0.05	83.99	86.18	88.73	91.52	84.89	87.28	84.92	78.87	84.01
0.10	87.94	90.85	92.60	92.12	88.72	87.89	86.53	85.67	88.00
0.50	92.34	92.92	94.53	94.86	91.93	92.70	91.85	89.42	88.76
1.00	92.58	94.30	94.74	95.55	93.66	93.91	94.64	91.51	89.97
1.50	93.04	94.47	94.96	95.72	95.85	93.97	94.05	92.91	90.29
2.00	93.27	94.65	95.06	95.80	96.08	94.04	94.10	94.13	89.40

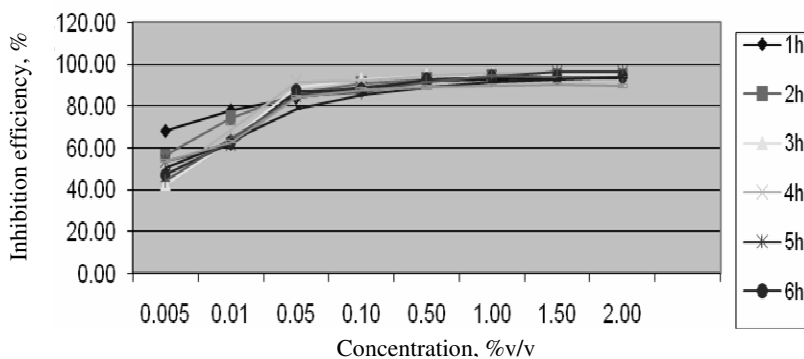


Figure 1. Variation of Inhibition efficiency of mild steel with various concentrations of MNP extract in 1 N HCl

Effect of immersion time

Inhibition efficiency of peel extract on mild steel is influenced by the immersion time. Inhibition efficiency of 93.27% was obtained for MNP extract for immersion period of 1 hour at 2% v/v concentration. At 3, 5 and 7h the maximum efficiency of 95.06%, 96.08% and 94.10% respectively were obtained for 2% v/v MNP extract (Table 1 and Figure 2). The variation in inhibition efficiency with increasing time may be due to the shift in adsorption and desorption equilibrium which takes place as the exposure time increases.

Effect of temperature

To study the effect of temperature on the corrosion inhibition properties of peel extract, experiments were carried out in absence and presence of varying concentration of the inhibitor

in the temperature range from 30-80 °C. The results are summarized in Table 2 and Figure 3. The data indicated that the peel extract was effective up to 40 °C and decreased slightly thereafter.

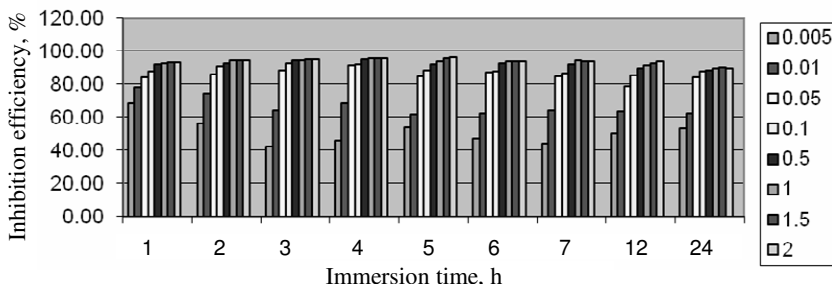


Figure 2. Influence of immersion time on inhibition efficiency of mild steel in various concentrations of MNP extract in 1 N HCl

Table 2. Effect of temperature on mild steel corrosion in 1 N HCl in absence and presence of MNP extract

Conc of extract, % v/v	Temperature, K					
	303	313	323	333	343	353
0.005	68.37	58.92	36.56	37.67	67.93	16.29
0.01	77.07	65.00	50.68	54.84	72.73	18.47
0.05	78.77	83.95	83.58	78.68	78.28	60.83
0.10	85.35	88.14	88.32	84.57	79.84	70.84
0.50	91.08	94.82	92.40	92.26	90.80	80.08
1.00	93.21	95.61	94.37	94.68	91.32	85.64
1.50	93.42	96.01	95.26	94.73	93.76	84.73
2.00	95.75	96.91	95.78	95.16	94.61	86.42

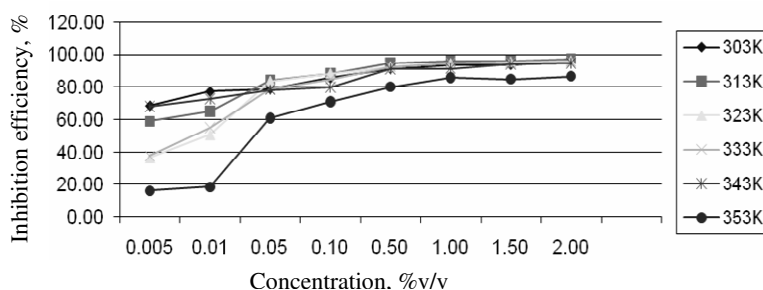


Figure 3. Effect of temperature on mild steel in 1 N HCl in presence and absence of MNP extract

The maximum efficiency of 96.91% at 40°C indicates that the inhibitor can be effectively used up to 40 °C. The decrease in inhibition efficiency with increase in temperature may be due to desorption of inhibitor molecules at faster rate at higher temperature^{13,27}.

Effect of surface coverage

The surface coverage θ of the inhibitor at different concentrations was calculated using the equation,

$$\theta = (1 - C_R / C_R')$$

Where, C_R and C_R' are the corrosion rate with and without inhibitor respectively obtained from the weight loss method.

The surface coverage increased with increase in the concentrations of extract. This may be due to increased number of inhibitor molecules getting parallelly adsorbed on the surface of mild steel²⁶.

Adsorption isotherm

The mechanism of corrosion inhibition and degree of adsorption of inhibitor depend on the chemical structure of the molecule, chemical composition of the solution, the nature of metal surface, the temperature and the electrochemical potential at the metal / solution interface. The surface coverage (θ) values help in understanding adsorption characteristics. The θ values for different concentrations of the extract were tested by fitting various isotherms such as Langmuir and Temkin.

Straight line obtained by plotting $\log(\theta / 1 - \theta)$ vs. $\log C$ (Langmuir adsorption) (Figure 4) and θ vs. $\log C$ (Temkin adsorption) (Figure 5) indicated that the process of inhibition is due to physical adsorption^{13,27,28}.

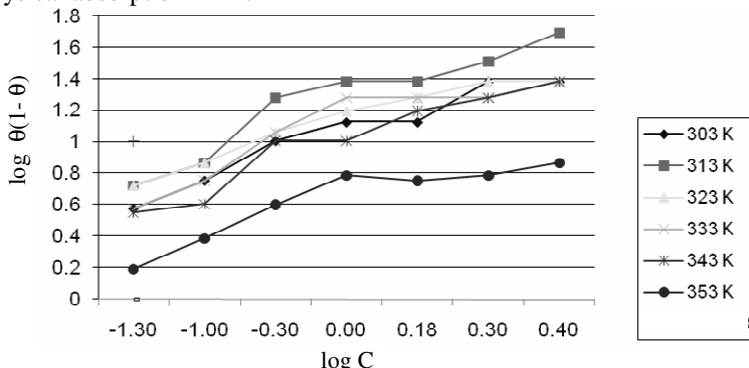


Figure 4. Langmuir adsorption isotherm of MNP extract on mild steel in 1 N HCl at various temperature

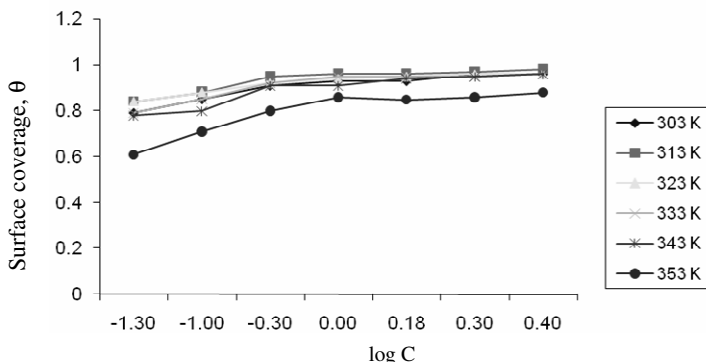


Figure 5. Temkin adsorption isotherm of MNP extract on mild steel in 1 N HCl at various temperature

Electrochemical method

Potentiodynamic polarization studies

The effect of the extract on the electrochemical behaviour of mild steel was studied by carrying out cathodic and anodic polarization experiments. The electrodynamic parameters

of the inhibitor such as corrosion potential E_{corr} , corrosion current density I_{corr} , anodic and cathodic Tafel slopes, b_a and b_c , in absence and presence of inhibitor are listed in Table 3 and depicted in Figure 6. Further the result reveals that I_{corr} values of acid in presence of inhibitor are lower than that of acid in absence of inhibitor indicating that increase in inhibition property was due to adsorption of inhibitor molecules on the electrode surface. This shows that the peel extract of *Musa acuminata* in 1N HCl acts as very good corrosion inhibitor for mild steel. The steady value of E_{corr} suggest that the inhibitor is mixed type inhibitor and this infers that the inhibitor reduces the hydrogen evolution and anodic dissolution of mild steel^{25, 29}.

Table 3. Potentiodynamic polarization parameters for mild steel in 1 N HCl in the absence and presence of MNP extract

Conc % v/v	$-E_{\text{corr}}$ V	I_{corr} mAmp/cm ²	b_c mV/dec	b_a mV/dec	Rp Ohm cm ²	% IE	
						Tafel	Linear
Blank	0.463	7831.0	774.19	317.84	8.204	-	-
0.005	0.455	2439.0	244.47	161.70	8.342	68.86	1.65
0.01	0.454	1235.0	219.13	121.99	8.948	84.23	8.31
0.10	0.464	118.7	170.84	101.56	18.010	98.48	54.45
0.50	0.466	124.8	196.33	75.57	18.651	98.41	56.01
1.00	0.459	130.1	191.83	68.18	20.283	98.34	59.55
1.50	0.468	64.1	176.57	71.79	26.503	99.18	69.05
2.00	0.472	65.7	167.35	77.64	26.526	99.16	69.07

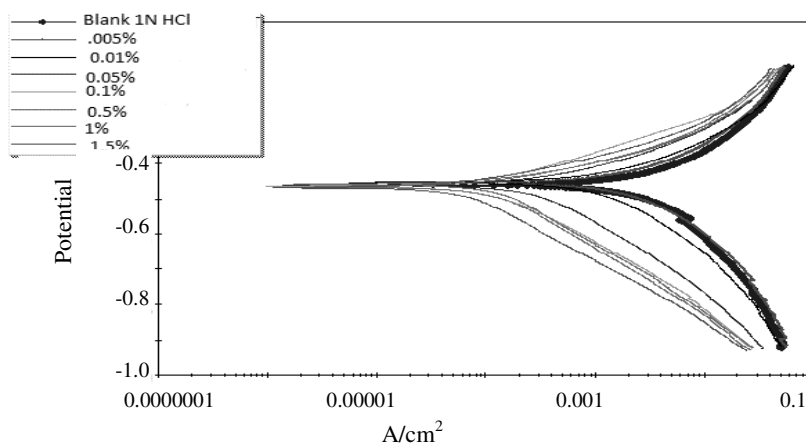


Figure 6. Potentiodynamic polarization curves for mild steel in 1 N HCl without and with different concentrations of MNP extract

Electrochemical Impedance studies (EIS)

The corrosion behaviour of mild steel in 1 N HCl in presence of MNP was also studied using EIS at 30 °C. The impedance parameters like charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and the corresponding inhibition efficiency are determined.

It is clear from the Table 4 and Figure 7 that C_{dl} values decreased with increase in concentration of the inhibitor which can result from decrease in dielectric constant due to adsorption of molecules of the extract on the surface of the metal¹². The R_{ct} values increase

with increase in the concentration of the inhibitor which are in accordance with the results obtained by weight loss method³⁰.

Table 4. EIS parameters for the corrosion of mild steel in 1 N HCl containing MNP extract at 30°C

Conc of extract % v/v	C_{dl} $\mu\text{F cm}^{-2}$	R_{ct} Ohmcm^2	%IE
Blank	2.298×10^{-9}	11.52	-
0.5	1.075×10^{-5}	88.11	86.93
1.0	1.308×10^{-5}	76.80	85.00
1.5	1.139×10^{-5}	144.70	92.04
2.0	1.593×10^{-5}	141.40	91.85

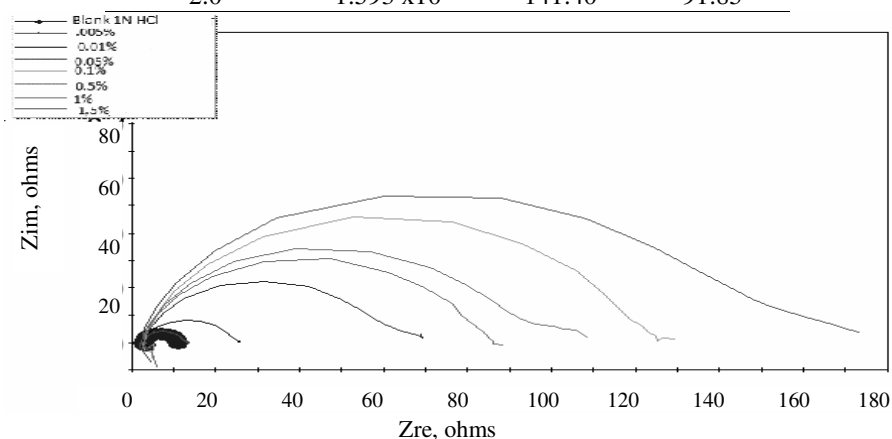


Figure 7. Impedance plots recorded for mild steel in 1 N HCl solutions without and with various concentrations of MNP extract

Corrosion inhibition mechanism

The peel extract of *Musa acuminata* (MNP) provides corrosion inhibition for mild steel by adsorption of the nutrients present in the extract which act as inhibitor molecules on the active sites on the metal surface. This is evident from Temkin adsorption isotherm where surface coverage (θ) is plotted against $\log C$. The plant nutrients sitosterol, stigmasterol, campesterol, cycloeucalenol, cycloartanol, and 24-methylene cycloartanol have either nitrogen or oxygen or both and pair of electrons in nitrogen and oxygen can facilitate the adsorption of the nutrients of the extract on metals. Interaction between the π electrons of oxygen and the vacant d orbital of the metal surface may also be another possibility for adsorption and for inhibition^{31,32}.

Conclusions

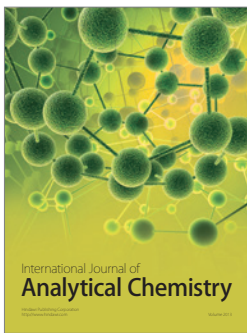
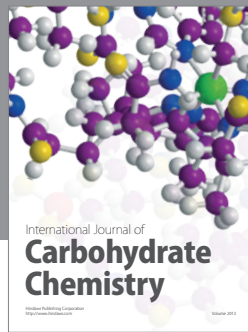
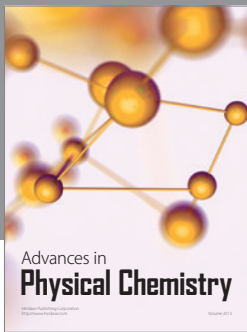
The peel extract of *Musa acuminata* was found to be effective inhibitor at concentration of 2% v/v in 1 N HCl solution. The inhibition efficiency of mild steel in 1 N HCl increases with increasing the concentration of MNP extract. The performance of the extract as corrosion inhibitor decreased with increasing temperature. AC impedance plots of mild steel in the acid medium show that polarization resistance increases with the increase of extract concentration. The results indicate that inhibition effect of the plant extract was due to physical adsorption of the nutrients present in the extract onto the active sites on the surface of the metal.

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