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Comparative Study of the Corrosion Inhibition and Adsorption of Ripe and Unripe Plantain (Musa paradisiaca) Peel Extract on Zinc in 2.0M CH_3COOH Acid Solution

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ABSTRACT

The aim of this study was to investigate the corrosion inhibition and adsorption of both ripe and unripe Musa paradisiaca peel on zinc sheet in 2.0M CH_3COOH acid solution. The corrosion inhibition study was carried out using weight loss study at temperatures of 303K, 313K and 323K. Comparatively the peel extract of the ripe Musa paradisiaca showed higher inhibition efficiency to corrosion than the unripe with tannins as the main difference in the constituents which has higher concentration of tannin in the ripe and very minute in the unripe. The inhibition efficiency of the both extracts was found to decrease with rise in temperature. The experimental data complied to the Henry, Flory-Huggins and Adejo-Ekwenchi isotherms amongst which the Henry Isotherm gave the best fit having the highest regression (R^2) values for both the ripe and unripe. The positive values of ΔH_{ads} and negative values ΔG_{ads} revealed the endothermic nature and spontaneity of the adsorption process respectively. Through the Kinetic-thermodynamic parameters such as E_a, ΔH_{ads}, ΔS_{ads}, ΔG_{ads} and the b parameter of the Adejo-Ekwenchi isotherm, the mechanism of adsorption was physiosorption.

Key Words: *Zinc, Corrosion, Musa paradisiaca, Adsorption Isotherm, Ethanoic acid.*

1.0 INTRODUCTION

Corrosion is the deterioration of metals in chemicals or reaction with its environment [6]. It is a ubiquitous phenomenon that deteriorates all materials, metals, plastics, glass and even concrete surfaces. Corrosion of metals can be considered as extractive metallurgy as it removes valuable metals from alloys. The study of zinc is a matter of tremendous theoretical and practical concern as it is widely used as an alloy to form important materials used in automobiles, electric components and household fixtures. Zinc as one of the most important nonferrous metals that has its extensive use in metallic coatings is amphoteric in its behavior towards acids and alkalis [7]. Zinc and zinc-coated products corrode rapidly in moist atmospheres forming white corrosion product-white rust.

Several inhibition methods for controlling corrosion attack has been reported and the use of inhibitors has proven to be effective and excellent in corrosion prevention. As a result of the toxicity, environmental restrictions and high cost of some inorganic inhibitors, the use of green inhibitors is being recently studied and a possible replacement of inorganic inhibitors. Organic compounds contain hetero atoms such as N, S, O, polar groups π electrons have been found to be very effective in inhibiting metallic corrosion when adsorbed on metallic surfaces [5]. This present study investigates the inhibiting, adsorption and thermodynamics of ripe and unripe *Musa paradisiaca* extract on zinc sheet corrosion in 2.0M CH_3COOH acid solution using weight loss measurement at 303K, 313K and 323K.

2.0 MATERIALS AND METHODS

2.1 Specimen Preparation

Rectangular pure zinc strips were used with dimension 80mm × 60mm × 0.5mm. The specimens were polished with emery paper, washed with deionized water, dried and weighed with an electronic balance to obtain their initial weights.

2.2 Preparation of extract

Fresh peels of ripe and unripe *Musa paradisiaca* were collected, washed, dried and pulverized into powdering form. The powdered extracts were Soxhlet extracted using ethanol and separated in a rotary evaporator at 80°C to obtain a solution free of ethanol. An aqueous aggressive solution of 2.0M Ethanoic acid was prepared. The stock solution was diluted with appropriate quantity of 2.0M Ethanoic acid to obtain inhibitor test solutions of 0.1-0.5g/l concentrations.

2.3 Weight loss test

Weight loss measurements was carried out on zinc strips at different temperatures of 303K, 313K and 323K. The dried samples were weighed and recorded before immersion into their respective solutions. The weight loss of the specimens was recorded every 5days for a period of 30 days. The corrosion rate, percentage inhibition efficiency and degree of surface coverage (θ) was calculated using the equations below:

$$C.R = \frac{87.6W}{\rho AT} \tag{1}$$

Where W is weight loss of zinc sheet (g), A is the total surface area of specimen in (cm^2), t is the exposure time in hours(hr) and ρ is specimen's density (g/cm^3).

$$\eta\% = \frac{CR_0 - CR}{CR_0} \times 100\% \tag{2}$$

where CR_0 and CR are the corrosion rates in (mm/yr) without and with different inhibitor concentrations.

$$\theta = \frac{CR_0 - CR}{CR_0} \tag{3}$$

3.0 RESULTS AND DISCUSSION

3.1. Phytochemical Analysis

Table 1: Phytochemical Composition of Ethanol extract of *Musa paradisiaca* peel

Phytochemical Constituents	% Composition of unripe peel	% Composition of ripe peel
Alkaloids	1.26 ± 0.051	1.37 ± 0.048
Tannins	0.001 ± 0.005	1.577 ± 0.004
Saponins	1.547 ± 0.0042	1.827 ± 0.0042
Flavonoids	1.321 ± 0.003	0.981 ± 0.0014
Glycosides	0.623 ± 0.002	0.351 ± 0.001

The results from Table 1 clearly reveals the phytochemical constituents present in the inhibitor acting as anti-corrosion agents are higher in concentrations in the ripe *Musa paradisiaca*.

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3.2 pH Measurement

The pH values of the 2.0M ethanoic acid, the ripe and unripe *musa paradisiaca* peel extract are shown in the table below:

Table 2. pH values of the 2.0M ethanoic acid, the ripe and unripe *musa paradisiaca* peel extract

Solvent	pH Value	Nature
Ethanoic Acid	2.6	Acidic
Unripe Peel Extract	6.2	Acidic
Ripe Peel Extract	6.3	Acidic

3.3. Weight loss

3.3.1 *Effect of temperature on Corrosion rate*

Table 3 and 4 shows calculated values of corrosion rates without and with inhibitor concentrations at different temperatures. It was observed that the corrosion rate decreases as the inhibitor concentration increases for both extracts. As the temperature increases, corrosion rate increases which is more pronounced in the unripe extract solution. This is because the ripe extract solution has a higher percentage of the phytochemical constituents thereby having a lower corrosion rate.

3.3.2 *Effect of temperature on Inhibition efficiency*

The results obtained from table 3 and 4 showed that increase in inhibitor concentration increases the efficiency of the both extracts. Increase in inhibitor concentration in the acidic medium resulted to adsorption of more active ions from the extracts on the surface of zinc strips and less contact of the zinc strips with the acidic environment, thereby increasing the inhibitor efficiencies. This supports the results obtained by [1]. From figure 1 and 2, it was observed that as temperature increases, the inhibition efficiencies of the ripe and unripe *Musa paradisiaca* extracts decreased, a trend often attributed to physical adsorption and vice versa for chemisorption [3]. Thus as temperature increases, the number of adsorbed molecules becomes less stable and decreases, leading to a decrease in the inhibition efficiency.

Table 3. Corrosion rate, Inhibition efficiency and Surface coverage of Unripe *Musa paradisiaca* at different temperatures

	303K			313K			323K		
Conc (g/l)	$CRx10^{-3}$ (mm/yr)	η%	θ	$CRx10^{-3}$ (mm/yr)	η%	θ	$CRx10^{-3}$ (mm/yr)	η%	Θ
Blank	0.802	__	__	1.268	__	__	1.484	__	__
0.1	0.343	57.23	0.572	0.573	54.81	0.548	0.722	51.35	0.514
0.2	0.287	64.21	0.642	0.487	61.59	0.616	0.610	58.89	0.589
0.3	0.230	71.32	0.713	0.403	68.22	0.682	0.519	65.03	0.650
0.4	0.172	78.55	0.786	0.315	75.16	0.752	0.408	72.51	0.725
0.5	0.114	85.79	0.858	0.226	82.18	0.822	0.300	79.78	0.798

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Table 4. Corrosion rate, Inhibition efficiency and Surface coverage of Ripe *Musa paradisiaca* at different temperatures

	303K			313K			323K		
Conc (g/l)	$CR\times10^{-3}$ (mm/yr)	η%	θ	$CR\times10^{-3}$ (mm/yr)	η%	Θ	$CR\times10^{-3}$ (mm/yr)	η%	θ
Blank	0.687	__	__	1.065	__	__	1.324	__	__
0.1	0.245	64.29	0.643	0.422	60.38	0.604	0.585	55.81	0.558
0.2	0.198	71.18	0.712	0.373	64.98	0.650	0.529	60.05	0.601
0.3	0.147	78.60	0.786	0.298	72.02	0.720	0.440	66.77	0.668
0.4	0.102	85.15	0.852	0.203	80.94	0.809	0.321	75.76	0.758
0.5	0.049	92.87	0.929	0.133	87.51	0.875	0.208	84.29	0.843

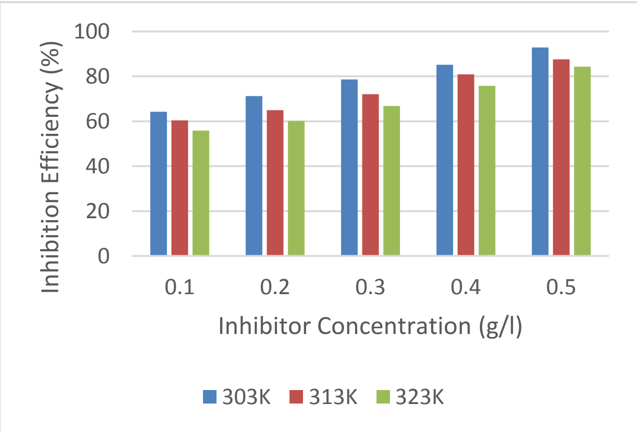

Fig 1. Inhibition efficiency vs Inhibitor concentration for Ripe *Musa paradisiaca*

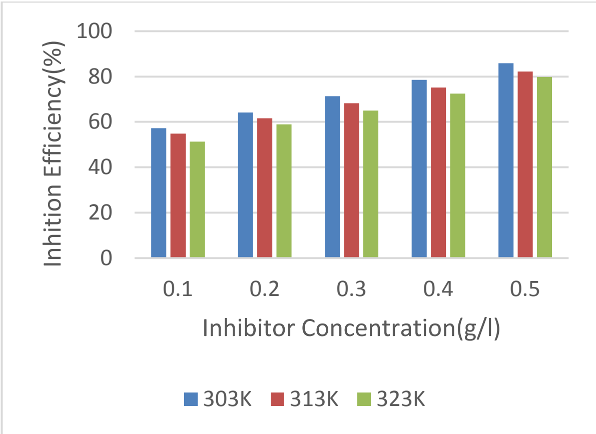

Fig 2. Inhibition efficiency vs Inhibitor concentration for Unripe *Musa paradisiaca*

3.4 Kinetics and Thermodynamic Model

The activation energy at different concentrations of ripe and unripe *Musa paradisiaca* extracts in 2.0M ethanoic medium was calculated by plotting Log CR against $\frac{1}{T}$ which gave linear graphs with slope equal to = $\frac{-E_a}{2.303R}$ and intercept equal to LogA using The Arrhenius type equation [4].

$$\text{Log CR} = \frac{-E_a}{2.303RT} + \text{LogA} \quad (4)$$

Where CR is the corrosion rate. E_a is the apparent activation energy (KJ/mol), T is absolute temperature (K), R is the universal gas constant (8.314J/MolK) and A is the pre exponential factor.

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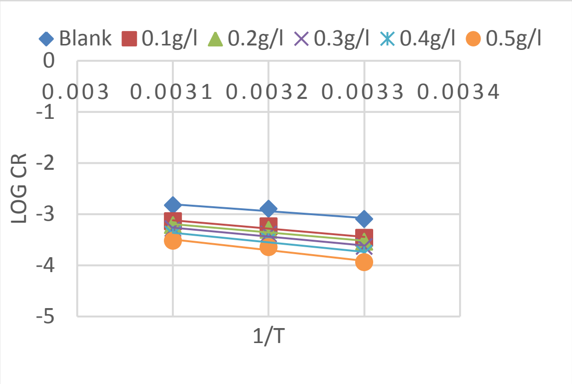


Fig 3: Variation of Log CR against ($\frac{1}{T}$) for Unripe *Musa paradisiaca* extract

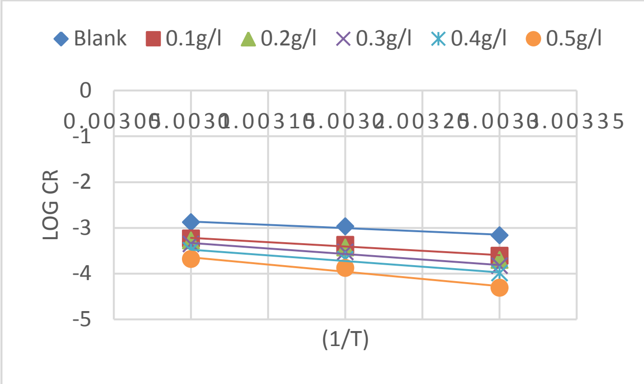
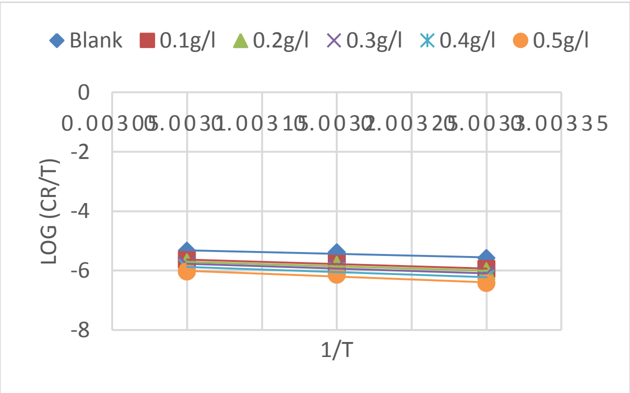


Fig 4: Variation of Log CR against ($\frac{1}{T}$) for Ripe *Musa paradisiaca* extract

The apparent activation energies for the both unripe and ripe extracts were calculated from the Arrhenius plots in Fig 3 and 4 respectively. The values of E_a as recorded in Table 5 was found to increase as the inhibitor concentration increases and higher than that of the blank indicating that the inhibitors inhibited the corrosion rate in the acidic media. Higher values of E_a in the presence of the inhibitors increases the energy barrier which decelerates the rate of corrosion on the zinc surface. The E_a values ranges from 25.19KJ/mol to 40.23KJ/mol (unripe) and 27.28KJ/mol to 60.10KJ/mol (ripe). The range of values of E_a are below the threshold value of 80KJ/mol which satisfies the trend for physisorption [9].

Table 5. Calculated values of corrosion kinetic and thermodynamic parameters for the corrosion of Zinc in 2.0M CH_3COOH without and with various concentrations of unripe and ripe *Musa parasidiaca* extract.

	Unripe *Musa paradisiaca*				Ripe *Musa paradisiaca*			
Conc (g/l)	$Ax10^2$ (g/cm^2hr)	E_a (KJ/mol)	ΔH_{ads} (KJ/mol)	ΔS_{ads} (J/mol)	$Ax10^2$ (g/cm^2hr)	E_a (KJ/mol)	ΔH_{ads} (KJ/mol)	ΔS_{ads} (J/mol)
Blank	0.18	25.19	22.93	-228.28	0.36	27.28	24.62	-204.09
0.1	0.77	30.94	28.	-217.71	4.38	36.19	33.53	-203.26
0.2	0.77	31.34	28.68	-217.81	22.88	40.86	38.21	-189.52
0.3	1.65	33.84	31.17	-211.43	111.56	45.59	42.92	-176.40
0.4	2.83	35.92	33.26	-206.93	174.02	47.66	45.01	-172.68
0.5	10.45	40.23	37.57	-196.06	12316.86	60.10	57.45	-137.26



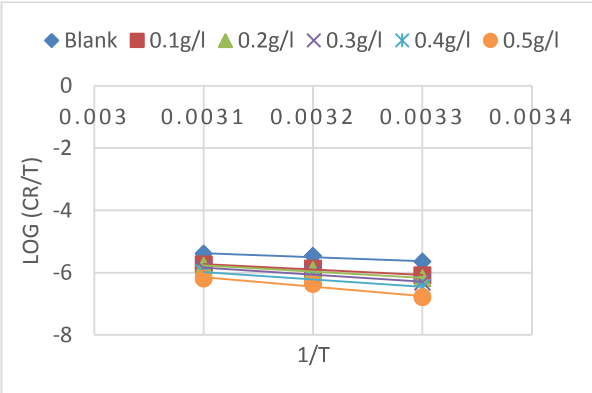


Fig 5. Variation of Log($\frac{CR}{T}$) against ($\frac{1}{T}$) for *paradisiaca* Ripe *Musa paradisiaca*

Fig 6. Variation of Log ($\frac{CR}{T}$) against ($\frac{1}{T}$) for Unripe *Musa*

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Thermodynamic parameters such as the Enthalpy (ΔH_{ads}) and Entropy (ΔS_{ads}) were calculated using the Eyring transition state equation shown below:

$$\text{Log}\left(\frac{CR}{T}\right) = \text{Log}\left(\frac{R}{Nh}\right) + \frac{\Delta S_{ads}}{2.303R} - \frac{\Delta H_{ads}}{2.303RT} \quad (5)$$

Where N is the Avogadro's number (6.2252×10^{23}) and h is the Planck's constant (6.6262×10^{-34}Js)

Fig 5 and 6 shows the plot of Log $\left(\frac{CR}{T}\right)$ against $\frac{1}{T}$ for both ripe and unripe *Musa paradisiaca* extract gave linear graphs with slope equal to $-\frac{\Delta H_{ads}}{2.303RT}$ and intercept equal to $\text{Log}\left(\frac{R}{Nh}\right) + \frac{\Delta S_{ads}}{2.303R}$. From Table 5, the positive values of the enthalpy of adsorption depicts the endothermic nature of the adsorption process. The large negative values of the entropy of adsorption indicates that the activated complex in the rate-determining step represents association rather than dissociation implying that disorderliness decreases ongoing from the reactants to the activated complex [8]. The results obtained is also in agreement with [2].

3.5 Adsorption Considerations

Adsorption isotherms play an important role in describing the adsorption behavior and nature of interactions of the extracts on metallic surfaces. The adsorption behavior of Ethanolic extract of both ripe and unripe *Musa paradisiaca* was studied by fitting the experimental data into Henry, Flory-Huggins and Adejo-Ekwenchi isotherms. The linearized forms for Henry, Flory-Huggins and Adejo-Ekwenchi isotherms are given by equation 6,7 and 8 respectively.

$$\text{Log}\,\theta = \text{Log}\,K_{ads} + \text{Log}\,C \quad (6)$$

$$\text{Log}\left(\frac{\theta}{C}\right) = \text{Log}\,K_{ads} + x\text{Log}(1-\theta) \quad (7)$$

$$\text{Log}\left(\frac{1}{1-\theta}\right) = \text{Log}K_{ads} + b\text{Log}C \quad (8)$$

Where x describes the number of molecules of the inhibitor adsorbed, b describes the mode of adsorption and K_{ads} represents the adsorption constant which is used to calculate the Gibbs free energy of adsorption from equation 9

$$\Delta G_{ads} = -2.303RT\text{Log}\,(55.5K_{ads}) \quad (9)$$

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Table 6. Parameters of various Adsorption Isotherms for Adsorption of Ethanolic extract of Unripe *Musa paradisiaca* on zinc surface

Isotherm	Temp (K)	Slope	Intercept		R^2	K_{ads}	ΔG_{ad} (KJ/m
Henry							
	303	0.2487	-0.0059		0.9643	0.9865	-10.09
	313	0.2473	-0.0249		0.9674	0.9443	-10.30
	323	0.2677	-0.0325		0.9709	0.9279	-10.59
Flory-Huggins				x			
	303	0.9817	0.9963	0.9817	0.8058	9.9152	-15.90
	313	1.1869	1.0349	1.1869	0.8264	10.8368	-16.66
	323	1.2316	0.9891	1.2316	0.8292	9.7521	-16.90
Adejo-Ekwenchi				b			
	303	0.6335	0.9448	0.6335	0.8548	8.8064	-15.60
	313	0.5384	0.8370	0.5384	0.8689	6.8707	-15.47
	323	0.5071	0.7783	0.5071	0.8736	6.0021	-15.60

Table 7. Parameters of various Adsorption Isotherms for Adsorption of Ethanolic extract of Ripe *Musa paradisiaca* on zinc surface

Isotherm	Temp (K)	Slope	Intercept		R^2	K_{ads}	ΔG_{ads} (KJ/mol)
Henry							
	303	0.2240	0.0216		0.9656	1.0510	-10.24
	313	0.2310	-0.0048		0.9261	0.9890	-10.42
	323	0.2512	-0.0223		0.9056	0.9499	-10.65
Flory-Huggins				x			
	303	0.6786	0.9679	0.6786	0.7581	9.2875	-15.74
	313	0.8967	0.9886	0.8967	0.7458	9.7409	-16.38
	323	0.9491	0.9184	0.9491	0.6929	8.2871	-16.48
Adejo-Ekwenchi				b			
	303	0.8927	1.2479	0.8927	0.8015	17.6970	-17.36
	313	0.6702	0.9984	0.6702	0.813	9.9632	-16.44
	323	0.5851	0.872	0.5851	0.7846	7.4473	-16.18

The regression value (R^2) obtained from the Henry's plot as recorded in table 6&7 were close to unity which was higher in the unripe extract showing that the sorption data followed Henry isotherm.

The parameter x of the Flory-Huggins isotherm describes the number of active sites occupied by one inhibitor molecule [10] adsorbed and has been shown from Table 7 for Ripe *Musa paradisiaca* to have values less than one indicating that more than one molecules of the inhibitor occupied one active site during the inhibition process. This is unlike the case of the unripe Musa

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paradisiaca extract having the x parameter to be less than one only at 303K. It shows that the Flory-Huggins model was more consistent with the ripe extract than the Unripe extract, therefore the unripe extract does not really fit into the model.

The Adejo-Ekwenchi isotherm model was used as a major determinant in describing the mode of adsorption from the calculated values of the b parameter. Decrease in the value of b with rise in temperature signifies physiosorption while increase or fairly constant value of b signifies chemisorption [10]. From Tables 6&7, the calculated values of the b parameter for the both extracts decreased with rise in temperature, clearly showing that the adsorption of ripe and unripe *Musa paradisiaca* extract onto the zinc surface was physiosorption.

The values of ΔG_{ads} calculated from the isotherm plots were all negative which showed the spontaneity of the adsorption process. Also the values of ΔG_{ads} were all found to be less than -20KJ/mol, a trend attributed to physiosorption.

4.0 CONCLUSION

Results from the present work shows that, ripe and unripe *Musa paradisiaca* extract were good corrosion inhibitors, with the ripe *Musa pardisiaca* extract giving the best inhibition efficiency over the unripe. The adsorption of the both extracts on zinc surface obeyed Henry, Flory-Huggins and Adejo-Ekwenchi Isotherms. The Henry isotherm gave the best fit having its regression values (R^2) for both extracts very close to unity compared to the Flory-Huggins and Adejo-Ekwenchi isotherms. The mechanism of physiosorption was proposed majorly from the b parameter of the Adejo-Ekwenchi isotherm, as well as from the calculated values ΔG_{ads}, ΔH_{ads} and the trend of inhibition efficiency with temperature. The positive values of the enthalpy of adsorption revealed that the inhibition is endothermic in nature accompanied by an increase in entropy.

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