ISSN No:-2456-2165

Musa Paradisiaca (Plantain) Stem Sap Extract as a Potential Corrosion Inhibitor on Mild Steel in Acid Medium

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Abstract:- This project compared both mechanically/manually extracted Musa paradisiaca stem sap sample and Soxhlet extracted sample. The result of the project shows that the average weight loss of the mild steel generally increased with a corresponding increase in time for both inhibited and uninhibited samples. Very low corrosion rate values were observed with the samples containing the inhibitor as compared to those without any inhibitor for both methods of extraction. Inhibition efficiency increased generally with increase in inhibitor concentration with optimum efficiencies of 76.43% for the manually extracted sap and 87.07% for the Soxhlet extracted sap. It was also established that Langmuir adsorption model best fit the experimental results with the manually extracted sample giving an R-Squared value of 0.9933 and the Soxhlet extracted sample giving an R-Squared value of 0.7331 after comparison of four different adsorption isotherms (Langmuir, Temkin, Freudlich and Florry-Huggins) at room temperature (27°C). The results obtained showed that the Soxhlet extracted sap was more efficient than the mechanically extracted sap.

Keywords:- *Musa paradisiaca; stem sap; corrosion inhibitor; mild steel.*

I. INTRODUCTION

Mild steel is a type of carbon steel with low carbon content also called low carbon steel. It is one of the most popularly used forms of steel as it possesses various characteristics such as ductility, magnetic and it is relatively cheap. It can be used for various industrial purposes. Mild steel is the major item of construction in the petrochemical industrial processes and other chemical industrial processes involving storage of acids. Mild steel is a more desired material than stainless steel because it is cheaper and more readily available than the later. Although it has low carbon content, it is quite strong. It is often used in structural steel applications and the transport of chemicals from one point to another. In the process industries, it is used for piping due to cost advantage. However, it is prone to the damaging effects of acid over time as it continuously interacts with acids [1, 2]. One method of reducing the damaging effects of these acids is the use of corrosion inhibitors.

Corrosion inhibitors are chemical compounds usually used in small concentrations whenever a metal is in contact with an aggressive medium [3, 4]. Plant extracts are a rich source of naturally synthesized chemical products, readily available, low-cost, and eco-friendly and can be obtained through simple extraction processes. Although many synthetic compounds show good corrosion inhibition ability, the search for more non-toxic, environment friendly inhibitors is the current focus in metallic corrosion. The efficiency of a corrosion inhibitor depends on fluid composition, quantity of water, and flow regime. A common mechanism for inhibiting corrosion involves formation of a coating, often a passivation layer, which prevents access of the corrosive substance to the metal. Permanent treatments such as chrome plating are not generally considered inhibitors, however.

Over the last few years, a good number of research findings on the use of plant extracts as green inhibitors has been published. The Musa species fall into this category. Reference [5] examined the effect of extract of *Musa paradisiaca* on corrosion inhibition of mild steel in aqueous 0.5 M sulphuric acid employing weight loss method, potentiodynamic polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency increased with increase in concentration of the extract but decreased with temperature. Potentiodynamic polarization result implied that *Musa paradisiaca* acts as a mixed-type inhibitor. SEM and AFM studies confirmed the adsorption of inhibitor molecules on the mild steel surface. The inhibition was assumed to follow Langmuir adsorption isotherm. Thermodynamic parameters indicated a strong interaction between the inhibitor and the mild steel surface. The inhibitory action of banana peel extract was investigated as well as a corrosion inhibitor in corrosion control of mild steel in 0.1M HCl solution [6]. Weight loss measurements and electrochemical techniques were used to perform the analyses. Surface analyses were also carried out using Fourier Transform Infrared (FTIR) spectroscopic techniques. The results indicated that inhibition efficiency increased as extract concentration increased. Reference [7] studied *Musa sapientum* (banana) peel extract as green corrosion inhibitor for mild steel in 1M HCl solution. The inhibition effect of the aqueous extract was investigated by weight loss measurement, electrochemical impedance spectroscopy (EIS), Tafel polarization and atomic force microscopy (AFM) techniques. Inhibition efficiency of the extracts decreased with maturity stages. Furthermore, the extracts were characterized by FTIR spectroscopy, UV–visible spectroscopy and high-performance liquid chromatography (HPLC) techniques. The mode of adsorption followed Langmuir adsorption isotherm model. The inhibition of the corrosion of mild steel by ethanol extract of *Musa sapientum* peels in H_2SO_4 was also studied utilizing the gasometric and thermometric methods [8]. The result of the study revealed that the different concentrations of ethanol extract of *Musa sapientum* peels inhibited mild steel corrosion. Inhibition efficiency of the extract varied with concentration, temperature, period of immersion and pH. Thermodynamic studies revealed that adsorption of the extract on the mild steel surface was spontaneous and occurred according to Langmuir and Frumkin adsorption isotherms. Physisorption was proposed for the adsorption of the inhibitor. Reference [9] investigated the inhibitive properties of *Musa Sapientum* peel extract as a green corrosion inhibitor for mild steel using factorial design method. The effects of two independent variables (concentration of banana peel extract and temperature) on the corrosion inhibition efficiency were examined using thermometric and gasometric techniques. The physicochemical properties of the extract such as surface tension, viscosity, flash point, and specific gravity were determined using standardized methods provided by the American System of Testing Materials (D-971). The statistical analysis of the inhibition efficiency was carried out using the Fit Regression Model of Minitab 17.0, while the fitness of the models was assessed by the coefficient of determination and the analysis of variance (ANOVA). Results showed that gasometric method gave a maximum inhibition efficiency of 66.83%, with an R^2 of 90.76%, while thermometric method gave a maximum inhibition efficiency of 65.70%, with an R^2 of 95.56%. The study shows that banana peel extract has the capacity to prevent the corrosion of mild steel in acidic medium. In another study, the inhibition efficiency of *Musa sapientum* peel extracts at different concentrations (300 – 500ppm) and temperatures (25°C to 60°C) on mild steel corrosion in 1M HCl acid using weight loss method was investigated [10]. Inhibition efficiency of the extract increased from 86.9% to 89.0% as the concentration of the extract increased but decreased with temperature. Gas chromatography-mass spectrometry (GC-MS) revealed the presence of bioactive compounds responsible for the corrosion inhibition and adsorption properties. FTIR analysis confirmed the presence of functional groups. The inhibitive properties of banana leaves water extracts (BLWE) as inhibitor for X70 steel corrosion in 1mol/L of HCl medium employing experimental and theoretical calculation methods were also examined [11]. Inhibition efficiency of up to 90% was obtained with addition of the extract. It was also established that BLWE is a mixed-type inhibitor. Surface morphology analysis also indicated that BLWE can effectually reduce the corrosion of X70 steel. The extract followed Langmuir adsorption isotherm. Quantum chemical (QC) calculation and molecular dynamics simulations (MDS) confirmed that (S)-2-amino-3-(4-hydroxyphenyl) propanoic acid (AHP), 3-(2-aminoethyl)-1H-indol-5-ol (ATI), and 3,4-Dihydroxycinnamic acid (DDA) in BLWE can exhibit excellent anti-corrosion properties. MDS results also showed that AHP, ATI and DDA can be adsorbed on the Fe (110) surface to obtain the maximum coverage. Reference [12] monitored the corrosion rate of mild steel in sulphuric acid, using *Musa paradisiaca* stem extract (MPSE) as corrosion inhibitor at temperatures of 303 and 333K. The corrosion rate and the inhibition efficiency were determined with gravimetric technique. Results revealed that *Musa paradisiaca* stem extract could serve as a corrosion inhibitor of mild steel in acidic media. The inhibition efficiency of MPSE recorded maximum values at lower temperature, increasing inhibitor concentration and decreasing concentration of corrodent. The sorption data gave adequate fit for Langmuir, Freundlich and Florry-Huggins isotherms.

This study compared the inhibitory properties of *Musa paradisiaca* stem sap extracted by mechanical/manual means and that extracted using n-hexane solvent on the corrosion of mild steel.

II. METHODS

A. Preparation of Mild Steel Coupons

The mild steel coupons with dimensions 3cm × 3cm × 0.05cm (length × width × thickness) were obtained from Centre for Industrial Studies (CIS), Federal University of Technology Owerri, (FUTO), Imo State, Nigeria. They were smoothened with sandpaper, soaked in acetone for degreasing and further cleaned with a brush. The coupons were weighed afterwards.

B. Preparation of the Extract

The extract was prepared in two ways: mechanical/manual extraction and solvent extraction (using a Soxhlet extractor). In the first method, the *Musa paradisiaca* stems were obtained from a farm at Eziobodo Elu, Owerri, Imo state after which they were cut into bits. The bits were then ground into paste using a mechanical grinder. The paste was sieved with Whiteman sieve. Five inhibitor test samples (10%, 20%, 30%, 40% and 50% of the extract in HCl solution) were prepared using volume per volume method.

In the second method, a Soxhlet extractor was used. This is made up of a glass body with round bottom distillation flask, a siphon arm, thimble, extraction chamber, and condenser (Fig. 1). The plantain stem from the farm was cut into smaller pieces and sun dried for 7 days.12g of the dried stem was placed in the thimble made from a strong fiber and placed in thimble chamber of the Soxhlet extractor apparatus. The round bottom flask containing 250ml of n-hexane was heated and the vapour produced flowed up the distillation path, into the main chamber and up into the condenser where it condensed and trickled down. The solvent then filled the main chamber, where it dissolved some of the desired compound from the solid sample. When the chamber was almost full, it was emptied by the siphon, returning the solvent to the round bottom flask to begin the process again.

ISSN No:-2456-2165

Fig. 1: Soxhlet Extraction setup

C. Qualitatative Phytochemical Analysis

The qualitative tests were carried out using the standard methods of analyses for alkaloids, flavonoids, tannins, saponins, steroids, terpenoids, phenols, oxalate, hydrogen cyanide and cardiac glycosides.

D. Weight Loss/Gravimetric Measurement

The volume per volume method was used to obtain 10%, 20%, 30%, 40% and 50% of the extract in 0.5M HCl solution. Six cylindrical, identical plastic containers were used for the experiment. Five of these containers were filled with a mixture of the acid solution and a defined concentration of the extract solution (V/V%) with the mild steel coupons immersed. The 6th of the containers was filled with pure acid solution and served as the control for the experiment. The volume of the solution in each container was 400ml. The coupons were observed daily for five days. At the end of each day, they were retrieved from the solution, dried, smoothened with sandpaper to remove rust particles, cleaned and then re-weighed. The weight loss was taken as the difference between the initial weight and the weight at any given time of observation. The weight loss data obtained were used to determine the corrosion rate and inhibition efficiency of the *Musa paradisiaca* stem sap extract.

Weight losses, corrosion rates, inhibition efficiencies and surface coverages were calculated from (1), (2), (3) and (4) respectively.

$$W_L = W_I - W_F \quad (1)$$

$$CR = W_I/(A \times t) \quad (2)$$

$$IE = (CR_O - CR_I/CR_O) \times 100 \quad (3)$$

$$\Theta = IE/100 \quad (4)$$

where
W_L = weight loss of coupon, g
W_I = initial weight of coupon, g
W_F = weight of coupon at any time of observation, g
CR = corrosion rate, g/cm^2day
A = area of coupon, cm^2
t = time of immersion, day
IE= inhibition efficiency, %
CR_O = corrosion rate of coupon before inhibition, g/cm^2day
CR_I = corrosion rate of coupon after inhibition, g/cm^2day
Θ = surface coverage

III. RESULTS AND DISCUSSION

A. FTIR Spectroscopy Analysis

The FTIR spectrum of the Musa paradisiaca was determined to identify the functional groups present in it. The result of the FTIR spectra of *Musa paradisiaca* stem sap extract is presented in Table 1. The peak value around $772.2033cm^{-1}$ was assigned to C-Cl stretching vibration of chloro compound. The peak around $1333.390cm^{-1}$ was assigned to C=C stretching vibration of ethene compound. The medium band around$1634.554cm^{-1}$ corresponds to NH stretching vibration of 1^0 amine compound. The peak around $1871.511cm^{-1}$ was attributed to CO stretching vibration of cyclic ester compound. The band around $2042.183cm^{-1}$ was assigned to COO anti-stretching vibration of carboxylic acid whereas the absorbance around $2485.979cm^{-1}$ corresponds to CN nitrile compound. The weak band around $2629.268cm^{-1}$ and $2811.049cm^{-1}$ correspond to C-H stretching vibration of methylene compound respectively. The broad bands around $3148.092cm^{-1}$ and $3538.102cm^{-1}$ were due to O-H stretching of 1^0 and 3^0 phenolic compounds respectively. This result confirms that the extract contains functional groups like (O-H) and (C=O). which meets the general characteristics of conventional corrosion inhibitors [13, 14].

Table 1: Interpretation of FTIR spectra of *Musa paradisiacal* stem sap extract.

S/N	Wavelength (cm^{-1})	Functional groups	Compounds
1	772.2033	C-Cl	Chloro Cl symmetric stretch
2	1373.390	H_2C=CH	Ethene CH anti-symmetric stretch
3	1634.554	RNH_3	1^0 amine NH stretch
4	1871.511	R-COO	Cyclic ester CO stretch
5	2042.183	RCOOH	Carboxylic acid CO stretch
6	2485.979	R- C=N	Nitriles CN anti-symmetric stretch
7	2629.268	CH_2	Methylene CH stretch
8	2811.049	CH_2	Methylene CH stretch
9	3148.092	RCHOH	1^0 alcohol OH stretch
10	3538.102	R_3CHOH	3^0 alcohol OH stretch

B. Qualitative Phytochemical Analysis

Phytochemical analysis of the extract confirmed the presence of alkaloids, flavonoids, tannins, saponins, steroids, terpenoids, phenols, oxalate, hydrogen cyanide and cardiac glycosides. The presence of these components in the extract enhanced the process of corrosion inhibitor adsorption on the mild steel as they have been reported to promote the corrosion inhibition of metals/alloys in aggressive acid media [15].

C. Weight Loss Analysis

Fig. 2 depicts that weight loss increased marginally with time of exposure for the solutions containing the extract except for the 40% v/v and 50% v/v samples whose profiles increased significantly between the 3rd and the 4th days of observation before decreasing again through the 5th day. It can also be observed that the weight loss values for the blank (control) medium were the highest. Fig. 3 gives the profiles for the Soxhlet extracted sap. There was a general increase in the weight loss profiles for this sample though the 10%, 30% and 50% v/v extracts showed slight decreases between the second and third days of observation. The 30% v/v extract also decreased between the 4th and 5th days of observation. However, results obtained from the solvent extraction method were generally lower than those obtained from the mechanical extraction method.

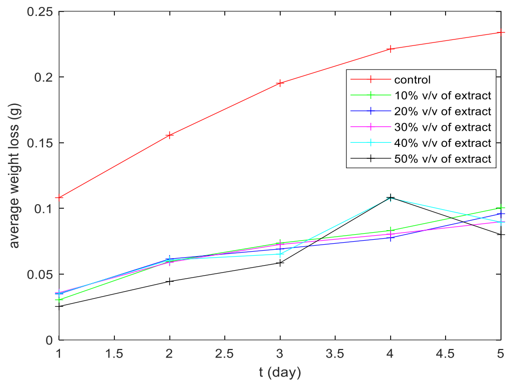

Fig. 2: Average weight loss against time at different extract concentrations (mechanical extraction method)

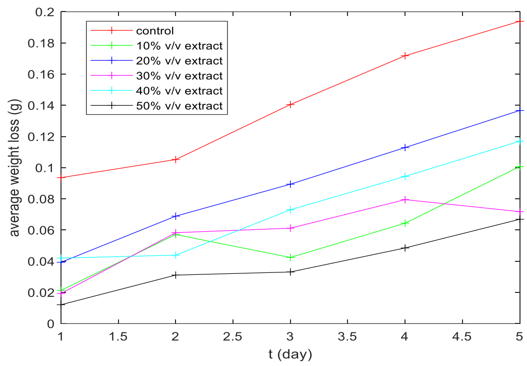

Fig. 3: Average weight loss against time at different extract concentrations (solvent extraction method)

D. Corrosion Rate Analysis

Fig. 4 and Fig. 5 show the graphs of corrosion rate against time for mechanically and solvent extracted *Musa paradisiaca* stem sap respectively. Examination of the plots reveals that corrosion rate values were higher in the blank medium than those containing the extract. For the manually extracted sap, the least corrosion rate was observed for the sample with the highest inhibitor concentration though it increased marginally on the fourth day of observation before reducing again. For the Soxhlet extracted sap, the least corrosion rate was experienced by the sample with the highest concentration throughout the period of experimentation. The Soxhlet extracted samples gave better results (lower corrosion rate values) when compared with the mechanically extracted samples. The low corrosion rates can be attributed to the adsorption of the molecules of sulfur, oxygen and nitrogen present in the phytochemical composition of the extract.

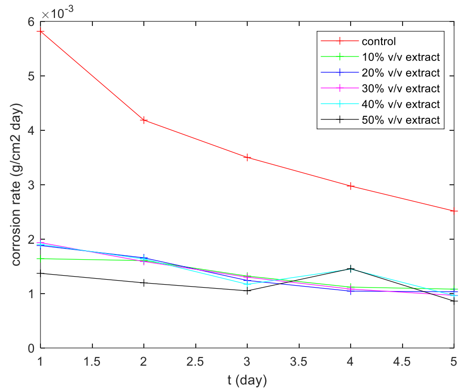

Fig. 4: Corrosion rate versus time at different extract concentrations (mechanical extraction method)

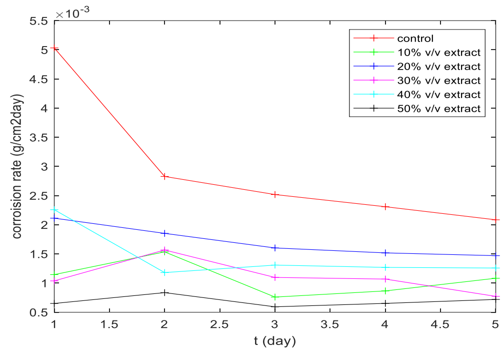

Fig. 5: Corrosion rate versus time at different extract concentrations (solvent extraction method)

E. Inhibition Efficiency

Inhibition efficiency is the measure of the effectiveness of an extract or inhibitor in reducing the corrosion rate of a substance. Tables 2 and 3 give the inhibition efficiency values for sap extracted by both methods. For the mechanically extracted sap the inhibition efficiency of the solution containing the highest concentration of 50% was higher than those of the other samples on every day of observation except for the 2nd and the 4th days. For the Soxhlet extracted sample, inhibition efficiency of the solution with the highest concentration was rather higher than those of the other samples throughout the period of experimentation. Optimum inhibition efficiencies obtained were 76.43% for the mechanically extracted sap and 87.07% for the solvent extracted sap.

Table 2: Inhibitor efficiency at different concentrations for mechanically extracted sap

Time (days)	Inhibitor Efficiency (%) for different extract concentrations (v/v)				
	10%	20%	30%	40%	50%
1	71.80	67.70	66.73	67.20	76.40
2	61.70	60.40	75.53	60.80	71.40
3	62.20	50.80	62.83	66.50	69.90
4	62.40	53.00	72.09	51.24	51.00
5	57.00	51.50	59.85	61.70	65.70

Table 3: Inhibitor efficiency at different Concentrations for Soxhlet extracted sap

Time (days))	Inhibitor Efficiency (%) for different extract concentrations (v/v)				
	10%	20%	30%	40%	50%
1	77.24	58.01	79.38	55.13	87.07
2	45.44	34.51	44.58	58.26	70.44
3	69.82	36.37	56.44	48.04	76.44
4	62.51	34.28	53.73	45.05	71.77
5	48.06	29.50	62.97	39.66	65.49

F. Adsorption Isotherm

Four different adsorption isotherms were tested in this study at room temperature (27°C), the Langmuir, Freundlich, Temkin and Flory-Huggins isotherms. A comparison of the adsorption isotherms showed that the Langmuir adsorption isotherm gave the best result with the R^2 values of 0.9933 and 0.7331 for the manually and Soxhlet extracted sap respectively.

IV. CONCLUSION

An investigation into the effect of *Musa Paradisica* stem sap extract on the corrosion inhibition of mild steel in 0.5M HCl was carried out in the present report for samples extracted by both mechanical/manual means and solvent technique. The result of the investigation shows that the average weight loss of the mild steel generally increased with a corresponding increase in time for samples extracted by both means. Very low corrosion rate values were observed with the samples containing the inhibitor as compared to those without any inhibitor for both methods of extraction. The inhibition efficiency (%IE) of the solution containing 50% extract concentration was generally higher than those of all other samples with the optimum of 76.43% obtained for the manually extracted sap and 87.07% obtained for the Soxhlet extracted sap. Higher values of inhibitor efficiency at 50% extract concentration indicates that more of the inhibitor molecules were adsorbed on the metal surface at a higher extract concentration thereby blocking the active sites of the metal. Again, Langmuir adsorption model best fit the experimental results with the manually extracted sap giving an R-Squared value of 0.9933 while that of the Soxhlet extraction gave an R-Squared value of 0.7331 after comparison of four different adsorption isotherms at room temperature (27°C).

V. ACKNOWLEDGMENT

The efforts of Mr Gerald Owoh of Chemical Engineering Departmental Laboratory, Federal University of Technology, Owerri, in making this piece of work a reality, by assisting with some laboratory experiments and explanations is highly appreciated.

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