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Studies on the Inhibitive Action of Musa Paradisiaca Stem Extrude on Corrosion of Mild Steel in an Acidic Medium

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Abstract:
The corrosion rate of mild steel was monitored in sulphuric acid, using Musa paradisiaca stem extrude (MPSE) as corrosion inhibitor at temperatures of 303 and 333K. The corrosion rate and the inhibition efficiency were determined with gravimetric technique. Results reveals that Musa paradisiaca stem extrude could serve as a corrosion inhibitor of mild steel in acidic media. The inhibition efficiency of Musa paradisiaca stem extrudes (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. The Gibbs free energy ranged between -4.488 to -3.237 kJmol^{-1}, activation energy ranged between 6.335 - 27.651kJ and the heat of adsorption ranged between - 2.282 to -2.776kJmol^{-1}. The results obtained shows that the inhibitive process is spontaneous, exothermic and a physisorption process.

Keywords: *MPSE, sulphuric acid, adsorption isotherm, corrosion*

1. Introduction

Corrosion of mild steel is of immense economic importance because mild steel is widely used in the fabrication of equipment and machineries used in various industrial processes. Mineral acids such as hydrochloric and sulphuric acids are also used in many of these industrial processes. The use of these acids results to substantial loss of the metals to corrosion (Oguzie, 2008; Rajendran and Karthikeyan 2012). Therefore, there have been concerted efforts to reduce this loss.

An important method employed to protect metals exposed to aggressive environment is by the use of corrosion inhibitors that reduce corrosion rate (Siragul *et al.,* 2010). Many inorganic compounds are very effective inhibitors of metal corrosion among which the chromate-based inhibitors are the most effective. However, their use is either restricted or banned as a result of their toxicity (Owate *et al.,* 2014). Thus, attention is now focused on the development of alternative nontoxic inhibitors. Among these alternatives are organic substances containing polar functional groups with nitrogen, sulphur, and/or oxygen in the conjugated systems (Siragul *et al.,*2010). Another alternative are natural products of plant origin which contain different organic compounds such as alkaloids, tannins, pigments, organic and amino acids that have corrosion inhibitive properties (Trease and Evans,1989). The use of natural products as corrosion inhibitors is of enormous interest because they are environmentally friendly, ecologically acceptable, readily available, inexpensive and renewable (Sofowara, 1993). Thus, the aim of this work is to study the corrosion inhibitory effect of MPSE as a natural corrosion inhibitor for mild steel in acidic media and fit the data obtained into different sorption isotherms in order to determine the type of adsorption.

2. Materials and Methods

The weight loss corrosion test method was used. The plantain stem extrude was collected (Rani and Basu, 2011) and filtered with a Whatmann number 42 filter paper. Phytochemical text was carried out using standard laboratory techniques (Durowaye *et al.,* 2014; Onuegbu *et al.,* 2013). 1.5M, 1.5M and 2.0M H_2SO_4 solution was used as the corrosive test solution at 303K and 333K. MPSEconcentrations of 10-50 (%v/v) were added to the corrosive test solutions. Prepared Mild Steel coupons were weighed thereafter suspended by suitable fiber threads and immersed in 100ml test solution. After 5 hours of immersion, each piece was taken out of the test solution, rinsed with distilled water, washed in acetone, dried and weighed again. A control was set up without adding MPSE. The corrosion rates (CR) were calculated using standard methods (Loto *et al*., 2013;Scendo and Uznanska, 2011)

3. Results and Discussion

Chemicals constituent	Score indication
Glycoside	-
Saponins	+
Flavonoids	-
Phenolics	+
Tannins	-
Eugenols	-
Steroids	-
Terpenoid	+
Alkaloids	++

Table 1: Phytochemical Screening of Musa Padisiaca Stem Extrude
+ = present ++ = largely present - = absent

Result from table 1 indicates that the corrosion inhibitory property of *MPSE* cannot be assigned to one particular Phytochemical.

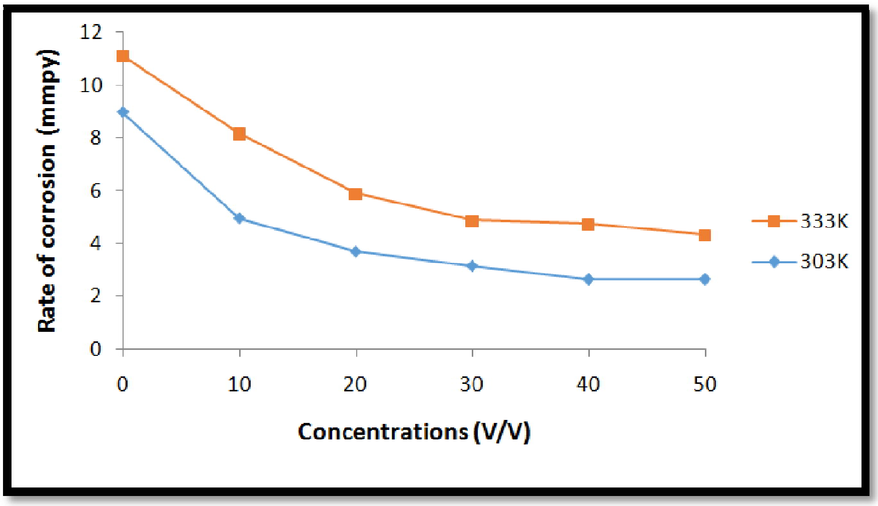

Figure 1: Effect of Inhibitor Concentration on Corrosion Rate

It was observed that the corrosion rate of mild steel decreases with increasing concentration of MPSE (Figure 1). The highest rate of corrosion was recorded in the blank and at higher temperature. This implies that the inhibitor is effective in retarding the corrosion of mild steel in acidic environments and that the extent of inhibition depends on the concentration of inhibitor present. The inhibition increased with increasing concentration of the MPSE

Result from the effect of corrodent (H_2SO_4) concentration on corrosion rate of mild steel at 303K (Table 2) reveals that the inhibition efficiencies (IE) decreased with increasing concentration of the acid corrodent. It is assumed that protonated inhibitor may exist as cationic species which may be adsorbed on the cationic sites of mild steel and reduce the evolution of hydrogen. As the acid concentration increases with the dissociation of inhibitor molecules getting completed, increase in acid concentration results in decrease in surface coverage due to increase in competition exerted by hydrogen ions getting adsorbed onto the mild steel, leading to evolution of hydrogen, that is, increased corrosion (Murthy and Vijayaragaven,2013).

Inhibitor conc. (%v/v)	1.0M H_2SO_4		1.5M H_2SO_4		2.0M H_2SO_4	
	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)
Blank	7.4460	-	9.0117	-	10.4371	-
10	3.2316	50.69	5.1024	43.38	6.5712	37.04
20	2.1899	70.59	3.8660	57.10	5.9711	42.79
30	1.8928	74.58	3.6056	59.99	5.3980	48.28
40	1.5145	79.66	2.9639	62.04	4.8459	53.57
50	1.1355	84.75	2.9639	67.11	4.7280	54.70

Table 2: Effect Corrodent (H_2SO_4) Concentration on Corrosion Rate of Mild Steel at 303K

The effect of inhibitor concentration on inhibition efficiency (Figure 2) revealed that the inhibition efficiency increased steadily as the inhibitor concentration increases up to inhibitor concentration of 50% v/v at both test temperatures. From the steep of the curve, it can be seen that the inhibition efficiency increased rapidly at lower concentrations, while at higher concentrations, the % IE remained more or less constant. Therefore, a further increase in inhibitor concentration will lead to no appreciable increase in %IE suggesting a complete surface coverage of the mild steel by the inhibitor molecules. It was also observed that the inhibition efficiency decreased with increase temperature. The decrease in inhibition efficiency with increase temperature may be due to desorption of the inhibitor molecules at faster rate at higher temperatures. This observation is in line with other research findings (Gunavathy and Murugavel, 2012).

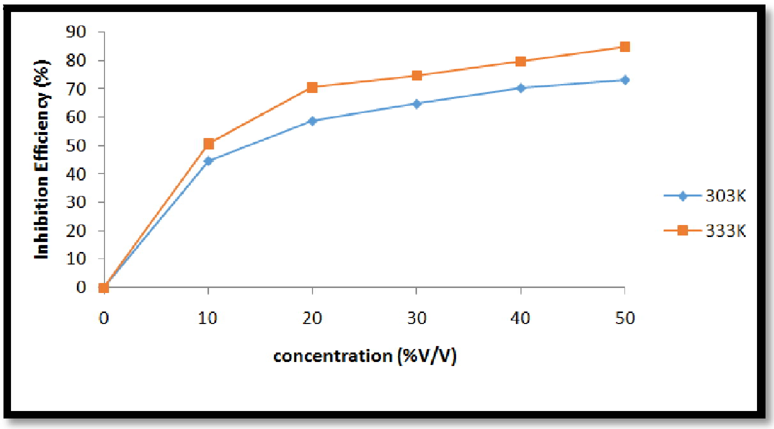

Figure 2: Effect of Temperature on Inhibition Efficiency of MPSE on Mild Steel in 1M H_2SO_4

Analysis of the temperature dependence of inhibition efficiency (Fig.2) as well as comparison of corrosion apparent activation energies in absence and presence of inhibitor gives some insight into the possible mechanism of inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature with concomitant increase in corrosion activation energy (*Ea*) in the presence of inhibitor compared to its absence suggests the formation of an adsorption film of physical nature. The reverse effect which is increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of inhibitor, suggests a chemisorptions mechanism. This means that decreased values of *Ea* from the non-inhibited solution indicate that the inhibition efficiency of the extract is greater at increased temperature, while increased values of *Ea* indicate that the inhibition efficiency of the extract reduces at increased temperature (Israel *et al.,* 2014).

In examining the effect of temperature on the corrosion process in the presence of the MPSE, the Arrhenius equation was used to calculate the activation energy of the process.

$$Log\left(\frac{\rho_2}{\rho_1}\right) = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Where *Ea* = apparent activation energy, *R* = molar gas constant, *T* = absolute temperature, *A*= Arrhenius constant, ρ_1 and ρ_2= corrosion rates at temperatures $T_1$and T_2respectively.The heat of adsorption was evaluated using the formula:

$$Q_{ads} = 2.303R\left[Log\left(\frac{\theta_2}{1-\theta_2}\right) - Log\left(\frac{\theta_1}{1-\theta_1}\right)\right] x \left(\frac{T_1T_2}{T_2 - T_1}\right)$$

$\theta_1$and θ_2 are the degrees of surface coverage at temperatures $T_1$and T_2 (Umoren *et al.,* 2008).

303K			**333K**			**Ea (KJmol^{-1})**	**Q_{ads} (kJ)**
Inhibitor conc. (%$^v/_v$)	**CR (mmpy)**	**Surface coverage θ**	**Inhibitor conc. (%$^v/_v$)**	**CR (mmpy)**	**Surface coverage θ**		
Blank	7.446	-		9.3388	-	6.335	-
10	3.2316	0.5069	10	5.9591	0.4865	17.115	-2.282
20	2.1899	0.7059	20	4.7955	0.5677	21.922	-.687
30	1.8928	0.7458	30	4.0372	0.6357	21.185	-1.453
40	1.5145	0.7966	40	3.4077	0.6351	22.680	-2.268
50	1.1355	0.8475	50	3.0519	0.6732	27.651	-2.776

Table 3: Activation Energy and Heat of Adsorption of MPSE on Mild Steel in 1M H_2SO_4

From Table 3it is evident that in all cases the values of Q_{ads} are negative. This shows that the adsorption process is exothermic. The higher values of Ea in the presence of MPSE compared to the control indicate that the inhibitor induces an energy barrier to corrosion reaction and this barrier increases with increasing concentration of the inhibitor. Therefore, the inhibitor adsorption efficiency decreases at higher temperature, thus supporting a physisorption mechanism (Durowaye *et al.*, 2014)

3.1. Adsorption Considerations

Basic information on the interaction between the inhibitors and the mild steel surface and mechanism of electrochemical reaction may be provided by adsorption isotherm (Murthy and Vijayaragavan, 2014). Adsorption isotherms are used to deduce whether the adsorption of the inhibitor molecules on the metal surface is by physisorption or chemisorption.

The adsorption of organic adsorbate on the steel surface is regarded as substitutional adsorption process between the organic compound in the aqueous phase (org) and the water molecules adsorbed on the steel surface $(H_2O)_{ads}$ (Zaafarany, 2013).

$Org\ (sol) + X(H_2O)\ Org_{(ads)} + XH_2O$

Where X is the size ratio, this is, the number of water molecules replaced by one organic molecule.

The sorption data obtained fitted into the Langmuir, Freundlich and Florry-Huggins isotherms.

3.2. Langmuir Adsorption Isotherm

According to the Langmuir isotherm, θ is related to the inhibitor concentration C (%v/v) by the following relation

$$\theta = \frac{k_{ads}C}{1 - k_{ads}C}$$

Where k_{ads} is the adsorption coefficient representing the interaction of inhibitor with a metal surface, C is the concentration of inhibitor and θ is the surface coverage. The linear form of equation is $\frac{C}{\theta} = \frac{1}{k_{ads}} + C$

A plot of $\frac{C}{\theta}$ against C will give a straight-line graph with the linear coefficient (intercept) equal to $1/_{k_{ads}}$.

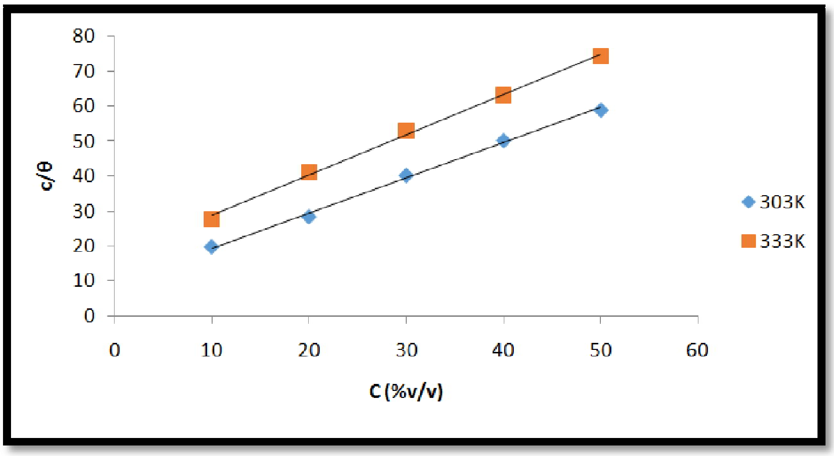

Figure 3: Plot of Langmuir Adsorption Isotherm of MPSE

The free energies of adsorption ΔG^0 were calculated from the adsorption coefficient.

$$k_{ads} = \frac{1}{55.5}\left[exp\left(-\frac{\Delta G^0_{ads}}{RT}\right)\right]$$

Where R is the gas constant (8.314kJ/mol) and T is the temperature in Kelvin. 55.5 is the concentration of water in solution in mol/L (Zaafarany, 2013).

The linear plots of C/θ versus C in different concentrations of inhibitor solutions in $1MH_2SO_4$ are displayed in Figures 3. The correlation coefficient is close to unity (between 0.996-0.999) at 303K and 333K. This indicates that the sorption data obtained fitted the Langmuir isotherm adequately. The deviation of the slope from unity is attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation (Durowaye *et al.,* 2014). The Langmuir isotherm assumes that the metal surface contains a fixed number of adsorption sites and each site holds one absorbate. The linear coefficient $(1/K_{ads})$ is used in the evaluation of K_{ads} and also ΔG^0.

Figure 3 shows a linear plot of Langmuir adsorption isotherm of MPSE in 1M H_2SO_4 with correlation coefficients close to unity. This shows that the adsorption between the inhibitor molecules and the metal surface is through a physisorption mechanism (Israel *etal.*, 2014).

Temperature	**Slope**	**R^2**	**K_{ads}**	**$\Delta G^0_{ads}(kJmol^{-1})$**
303K	1.004	0.997	0.107	-4.488
333K	1.151	0.997	0.058	-3.327

Table 4: Langmuir Adsorption Parameters

It can be seen from Table 4 that the values of k_{ads} are low. This means that the interaction between molecules of MPSE with the mild steel in 1M H_2SO_4 at 303Kand333K are weak. The negative values of ΔG^0_{ads} for MPSE indicate that the adsorption process is spontaneous and the adsorbed layer on the mild steel surface is stable. Generally, the value of -

20kJ/mol for ΔG^0_{ads} or lower is consistent with physisorption (Onuegbu *et al.*, 2013). It also confirmed the feasibility of the sorption process (Obot *et al.*, 2012).

3.3. Freundlich Adsorption Model

Freundlich adsorption isotherm is given by the equation: $\theta = KC^n$ or in the logarithmic form $\mathbf{Log\ \theta = log\ K + n\ log\ C}$

K (the adsorption capacity) and C represent the equilibrium constant of adsorption process and additive concentrations respectively. A plot of log θ against log C will give a slope of n and intercept equal to log K. n is the intensity of adsorption.

Figure 4 shows Freundlich isotherm plot for MPSE extrude adsorption on mild steel surface in 1M H_2SO_4. The trends have correlation coefficients which are approximately equal to unity.

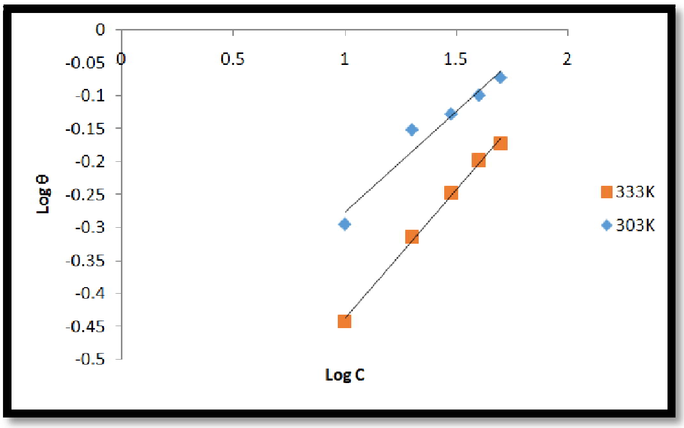

Figure 4: Freundlich Adsorption Isotherm Plot of Mpsein 1M H_2SO_4at 303K and 333K

Temperature	Slope	R^2	K_{ads}	N
303K	0.306	0.947	0.261	0.306
333K	0.390	0.996	0.149	0.390

Table 5: Freundlich Adsorption Parameters

The results in Table 5 show that the adsorption capacity (K) and the intensity of adsorption (n) are low. Therefore, the adsorption of molecules of MPSEon to the active sites of the mild steel is weak.

3.4. Florry-Huggins Isotherm

The substitution of water molecules by inhibitor forms the basis of assumption in Florry Huggins isotherm. The equation of Florry–Huggins isotherm is given by:

$$\frac{\boldsymbol{\theta}}{[\boldsymbol{e}^{(x-1)}](\mathbf{1}-\boldsymbol{\theta})^{x}} = \boldsymbol{k_{ads}C}$$

A linear form of the equation can be written in the form $log\frac{\theta}{C} = xlog(1-\theta) + logk$.where θ is the degree of surface coverage and x is the number of active sites occupied by one inhibitor molecule (Horsfall and Spiff, 2004).
A plot of $log\,\theta/C$ against $log(1-\theta)$ will give a straight-line graph with slope of x and intercept of$logk$ which allows x and k to be evaluated.

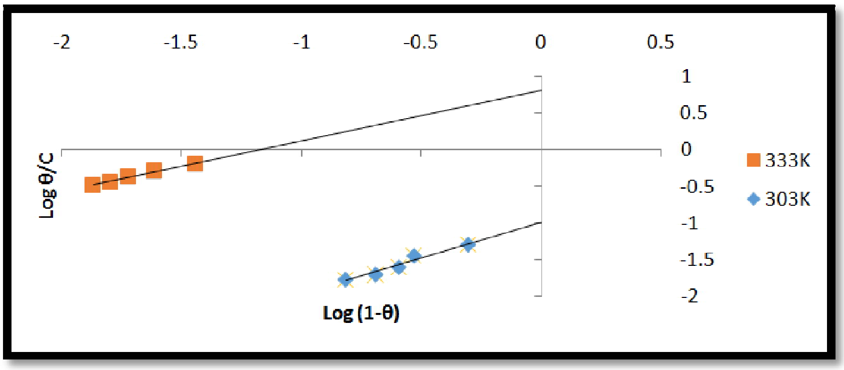

Figure 5: Florry-Huggins Adsorption Isotherm Plot of Mpsein 1M H_2SO_4at 303K and 333K

Temperature	slope	R2	Kads	X
303K	0.979	0.988	0.103	0.979
333K	0.687	0.958	6.397	0.687

Table 5: Florry-Huggins Parameters

Table 5 shows that the number of water molecules which one inhibitor molecule is able to displace decreases with increase in temperature. This corroborates the earlier result obtained that inhibition efficiency of MPSE on corrosion of mild steel decreases as temperature increases.

3.5. Specific Reaction Rate

The equation that correlates specific reaction rate (k) with corrosion rate (r) is given by

$$Lnr = Lnk + BC$$

Where B is a constant and C the concentration of the corrosive medium (Murthy and Vijayaragavan,2014).
When lnr is plotted against C the intercept gives lnk from which the specific rate of reaction was calculated

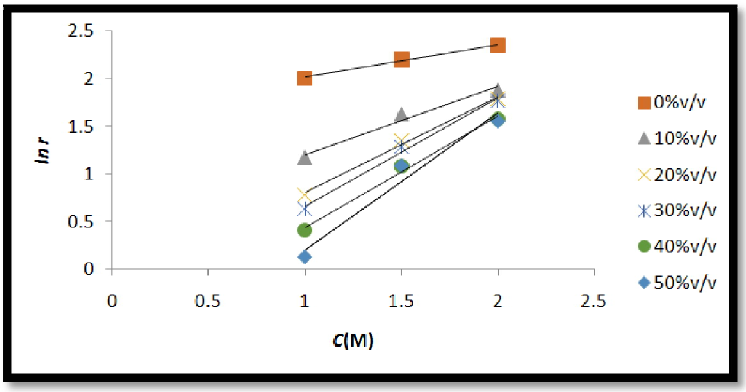

Figure 6: Plot of lnr against C

Inhibitor Conc. ($\%^{v}/_{v}$)	0	10	20	30	40	50
K($mgcm^{-2}h^{-1}$)	5.349	1.645	0.822	0.631	0.488	0.296

Table 6: Specific Reaction Rate of Corrosion in H_2SO_4

The specific rate of reaction, k, of the in the corrodents containing the inhibitor was found to be generally low. The specific reaction rate of the mild steel in the uninhibited solution was far greater than that containing the inhibitor. The specific reaction rate decreases as the concentration of the inhibitor increases.

4. Conclusion

MPSE was found to inhibit the corrosion of mild steel in sulphuric acid. The inhibitor was found to give adequate fit for Langmuir, Freundlich and Florry-Huggins adsorption isotherms. This reveals that the mechanism of adsorption is physisorption. Based on the kinetic and thermodynamic parameters that were obtained from sorption data the adsorption of the inhibitor was found to be feasible, spontaneous and exothermic in sulphuric acid. This study provides new information on corrosion inhibitory potential of MPSE on mild steel in acidic environments at 303K and 333K.This green corrosion inhibitor could find possible application in industrial steel pickling processes.

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